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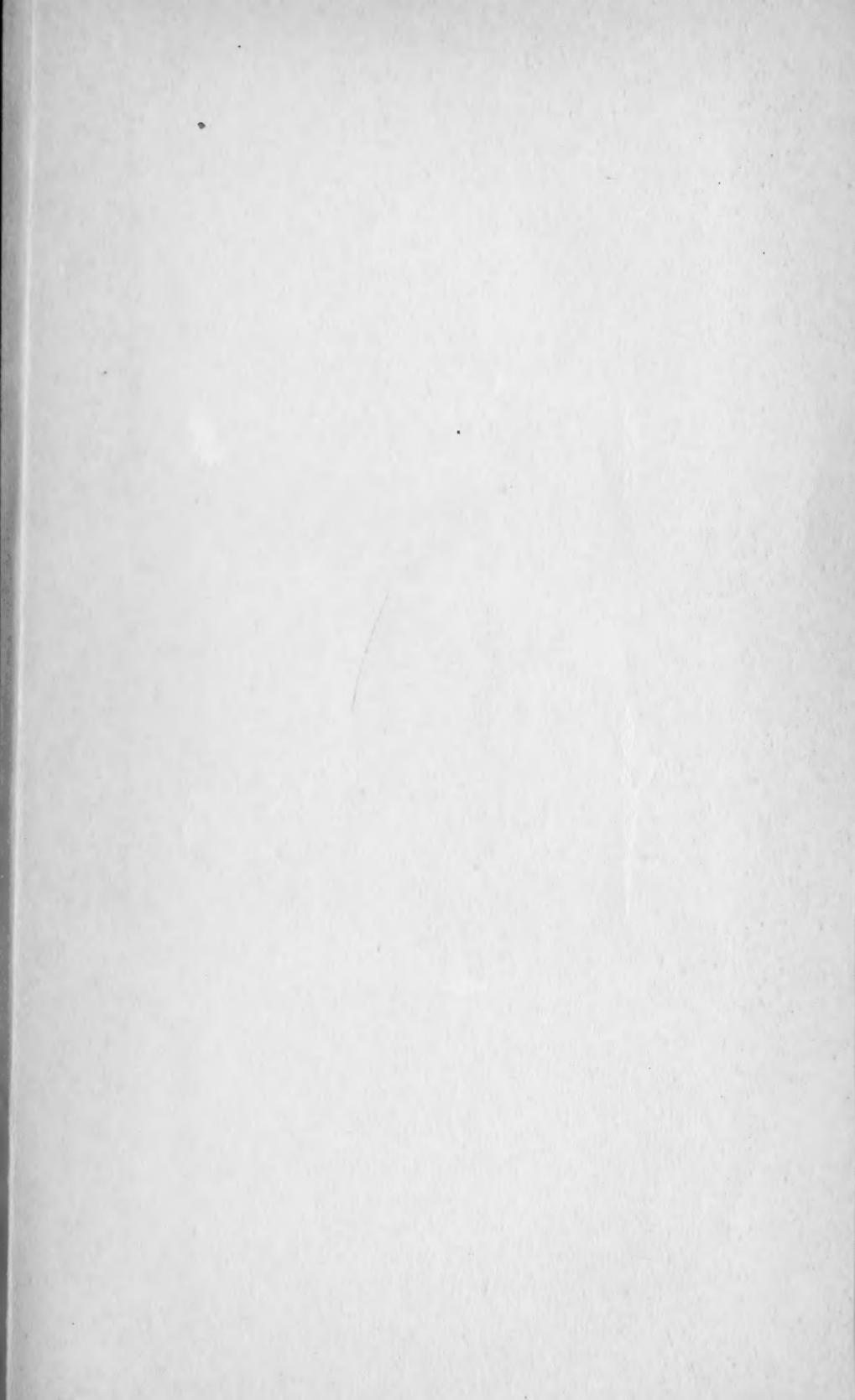
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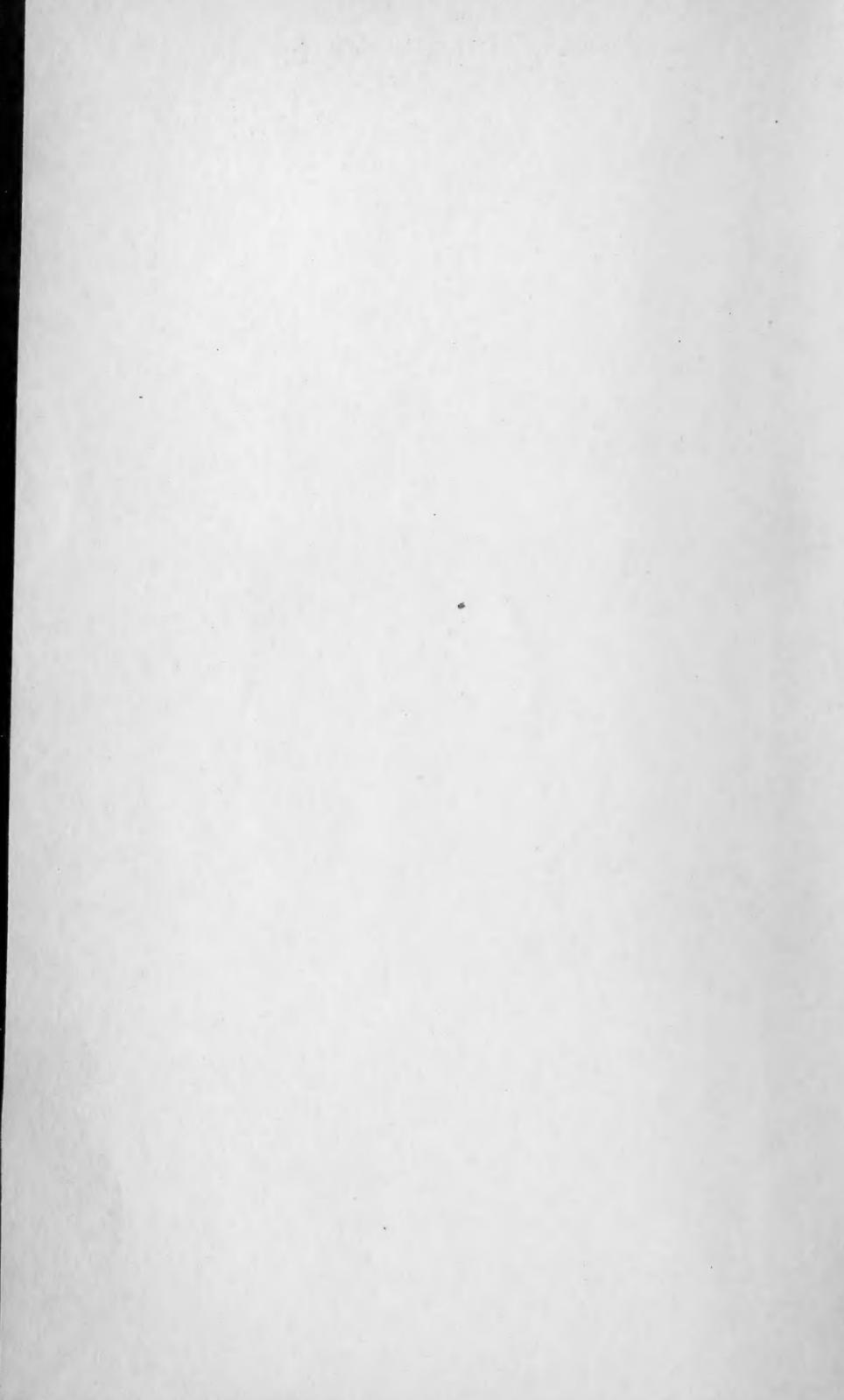


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AND  
WILLIAM FRANCIS, Ph.D. F.L.S. F.R.A.S. F.C.S.

"Nec aranearum sane textus ideo melior quia ex se filia gignunt, nec noster  
vilius quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. 1. Not.*

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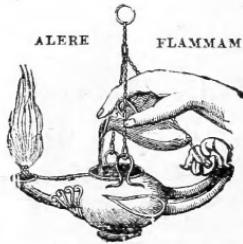
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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

---

—“Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condat,  
Quid toties diros cogat flagrare cometas,  
Quid pariat nubes, veniant cur fulmina cœlo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu.”

*J. B. Pinelli ad Mazonium.*



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#### ERRATUM.

Page 11. In the first column of Table IV. all the decimal points except the first should be omitted, and the column should stand :

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etc.

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THE

# KINETIC THEORY OF GASES

ELEMENTARY TREATISE  
WITH MATHEMATICAL APPENDICES

BY

DR OSKAR EMIL MEYER

PROFESSOR OF PHYSICS AT THE UNIVERSITY OF BRESLAU

*TRANSLATED FROM THE SECOND REVISED EDITION*

BY

ROBERT E. BAYNES, M.A.

STUDENT OF CHRIST CHURCH, OXFORD, AND DR LEE'S READER IN PHYSICS

## TRANSLATOR'S PREFACE

HAVING found the first edition of this book of great use, I have willingly undertaken the preparation of an English translation of this greatly enlarged and improved second edition. I have embodied in it all the additional matter contained in the Addenda to the German text, as also certain modifications and additions communicated to me by Professor Meyer, who, by reading the proofs, has ensured their accuracy.

It has been no part of my intention to add any commentary upon the book, but I have appended a few foot-notes that seemed advisable, and I have added an Index which I hope will prove useful.

ROBERT E. BAYNES

OXFORD : October 1899

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1899

# AUTHOR'S PREFACE

TO  
THIS EDITION

THE first edition of this book appeared in 1877, at the time of the most rapid and beautiful development of the kinetic theory of gases. About twenty years before, the founders of the theory, Krönig and Clausius, had explained the expansive tendency of gases, and had calculated their pressure on the assumption that the smallest particles of gases do not repel each other, but are in rapid motion. From the theory based on this supposition not only were the laws of gases, so far as they were then known, deduced in simplest fashion, but also new laws, hitherto undreamt of, were discovered, which were afterwards confirmed when tested by experiment. These results, which we owe to Maxwell and Clausius, quickly won to the theory many friends and adherents.

But a deeper insight into the new theory was not then widely possessed, since the mathematical shape of the memoirs formed a grave obstacle for many readers. I undertook therefore to exhibit the kinetic theory of gases in such a way as to be more easily intelligible to wider circles, and especially to chemists and other natural philosophers to whom mathematics are not congenial. To this end I endeavoured, much more than was otherwise usual, not only to develop the theory by calculation, but rather to support it by observation and found it on experiment. I therefore collected together, as completely as I could, and summarised, the observations by which the admissibility of the theory might be tested and its correctness proved. I dare to think that I have not failed in this endeavour ; for not only did my book receive favourable judgment, but also my presentation of the subject was turned to much account in popular writings and found its way into physical textbooks.

In this my book fulfilled the purpose I intended. I wrote it only for that time, and did not seriously think that it might

## AUTHOR'S PREFACE TO THIS EDITION

reappear in a new edition after long years. But the demand for the book did not cease, and, as the supply was nearly exhausted more than ten years ago, I had to determine on a revision, although the necessary preliminary work had not yet been done.

As to the general plan of the revision I could not long be in doubt. I could not destroy the shape in which the book had been proved and had won recognition, and I have therefore written it anew on the old plan. The mathematical discussions form, as before, an Appendix which makes no claim to completeness and need not be studied by every reader; the contents of the book are limited to the same range of phenomena as in the first edition; the observations which I have taken into consideration belong partly to mechanical physics and partly to the domains of heat and chemistry. The book has therefore preserved its character, and may perhaps also serve its first purpose.

I have inserted a series of new theories, as for instance, an explanation on the kinetic theory of the resistance of air and of the reaction of a jet, together with a longer investigation, also new, concerning the influence of the dissociation of the molecules of a vapour upon its viscosity. I should have enlarged the contents of the book in many other directions with pleasure; I should gladly, for instance, have treated of evaporation in connection with the diffusion of gases and have discussed many other subjects allied to the gaseous theory. But I had to omit much, since the work would have demanded too much time. With the present limitation to the old range it has cost very much trouble and very much time to work up the literature of the subject, that has grown mightily in these more than twenty years.

The first German edition of this book has already had a large sale in England and America. The present English translation will contribute to a still wider dissemination of the book, and will win new friends to the kinetic theory. This I confidently hope, now that by reading the proofs I have seen the loving care with which Mr. Baynes has worked at the translation. By numerous suggestions, too, he has enabled me to remove some errors and to make corrections and additions. For this I here express to him my warmest thanks.

OSKAR EMIL MEYER

BRESLAU: September 1899

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[FIFTH SERIES.]

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JANUARY 1900.

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- I. *A Radio-active Substance emitted from Thorium Compounds.*  
By E. RUTHERFORD, M.A., B.Sc., Macdonald Professor of Physics, McGill University, Montreal \*.

IT has been shown by Schmidt† that thorium compounds give out a type of radiation similar in its photographic and electrical actions to uranium and Röntgen radiation. In addition to this ordinary radiation, I have found that thorium compounds continuously emit radio-active particles of some kind, which retain their radio-active powers for several minutes. This "emanation," as it will be termed for shortness, has the power of ionizing the gas in its neighbourhood and of passing through thin layers of metals, and, with great ease, through considerable thicknesses of paper.

In order to make clear the evidence of the existence of a radio-active emanation, an account will first be given of the anomalous behaviour of thorium compounds compared with those of uranium. Thorium oxide has been employed in most of the experiments, as it exhibits the "emanation" property to a greater degree than the other compounds; but what is true for the oxide is also true, but to a less extent, of the other thorium compounds examined, viz., the nitrate, sulphate, acetate, and oxalate.

In a previous paper ‡ the author has shown that the radiation

\* Communicated by Prof J. J. Thomson, F.R.S.

† Wied. Ann. May 1898.

‡ Phil. Mag. Jan. 1899, p. 109.

from thorium is of a more penetrating character than the radiation from uranium. Attention was also directed to the inconstancy of thorium as a source of radiation. Owens\* has investigated in more detail the radiation from thorium compounds. He has shown that the radiations from the different compounds are of the same kind, and, with the exception of thorium oxide in thick layers, approximately homogeneous in character.

The intensity of thorium radiation, when examined by means of the electrical discharge produced, is found to be very variable; and this inconstancy is due to slow currents of air produced in an open room. When the apparatus is placed in a closed vessel, to do away with air-currents, the intensity is found to be practically constant. The sensitiveness of thorium oxide to slight currents of air is very remarkable. The movement of the air caused by the opening or closing of a door at the end of the room opposite to where the apparatus is placed, is often sufficient to considerably diminish the rate of discharge. In this respect thorium compounds differ from those of uranium, which are not appreciably affected by slight currents of air. Another anomaly that thorium compounds exhibit is the ease with which the radiation apparently passes through paper. The following table is an example of the way the rate of leak between two parallel plates, one of which is covered with a *thick* layer of thorium oxide, varies with the number of layers of ordinary foolscap-paper placed over the radio-active substance.

TABLE I.

Thickness of each Layer of Paper = .008 cm. 50 volts  
between plates.

Number of Layers of Paper.	Rate of Discharge.
0	1
1	.74
2	.74
5	.72
10	.67
20	.55

\* Phil. Mag. Oct. 1899, p. 360.

In the above table the rate of leak with the thorium oxide uncovered is taken as unity. It will be observed that the first layer reduced the rate of leak to .74, and the five succeeding layers produce very little effect.

The action, however, is quite different if we use a *thin*\* layer of thorium oxide. With one layer of paper, the rate of discharge is then reduced to less than  $\frac{1}{6}$  of its value. At first sight it appears as if the thorium oxide gave out two types of radiation, one of which is readily absorbed by paper, and the other to only a slight extent. If we examine the radiation given out by a thin layer of thorium oxide, by placing successive layers of thin paper upon it, we find the radiation is approximately homogeneous, as the following table shows.

TABLE II.  
Thickness of Paper = .0027 cm.

Number of Layers of Thin Paper.	Rate of Discharge.
0	1
1	.37
2	.16
3	.08

The rate of leak of the bare salt is taken as unity. If the radiation is of one kind, we should expect the rate of discharge (which is proportional to the intensity of the radiation) to diminish in geometrical progression with the addition of equal thicknesses of paper. The above figures show that this is approximately the case. With a thick layer of thorium oxide, by adding successive layers of thin paper, we find the rate of discharge gradually diminish, till after a few layers it reaches a constant value. The amount that is cut off by the first layer of foolscap-paper (see Table I.) is of the same kind of radiation as that which is emitted by a thin layer of oxide.

On directing a slight current of air between the test-plates, the rate of discharge due to a thick layer of thorium oxide is

\* To produce a thin layer on a plate, the oxide, in the form of a fine powder, was sprinkled by means of a fine gauze, so as to cover the plate to a very small depth. By a thick layer is meant a layer of oxide over a millimetre in thickness.

greatly diminished. The amount of diminution is to a great extent independent of the electromotive force acting between the plates. Under similar conditions with uranium, the rate of leak is not appreciably affected. With a thin layer of oxide, the diminution of the rate of leak is small; but with a thick layer of oxide, the rate of leak may be reduced to less than one-third of its previous value. If two thicknesses of foolscap-paper are placed over the thorium oxide, the resulting rate of leak between the plates may be diminished to less than  $\frac{1}{20}$  of its value by a slight continuous blast of air from a gasometer or bellows.

The phenomena exhibited by thorium compounds receive a complete explanation if we suppose that, in addition to the ordinary radiation, a large number of radio-active particles are given out from the mass of the active substance. This "emanation" can pass through considerable thicknesses of paper. The radio-active particles emitted by the thorium compounds gradually diffuse through the gas in its neighbourhood and become centres of ionization throughout the gas. The fact that the effect of air-currents is only observed to a slight extent with thin layers of thorium oxide is due to the preponderance, in that case, of the rate of leak due to the ordinary radiation over that due to the emanation. With a thick layer of thorium oxide, the rate of leak due to the ordinary radiation is practically that due to a thin surface-layer, as the radiation can only penetrate a short distance through the salt. On the other hand, the "emanation" is able to diffuse from a distance of several millimetres below the surface of the compound, and the rate of leak due to it becomes much greater than that due to the radiation alone.

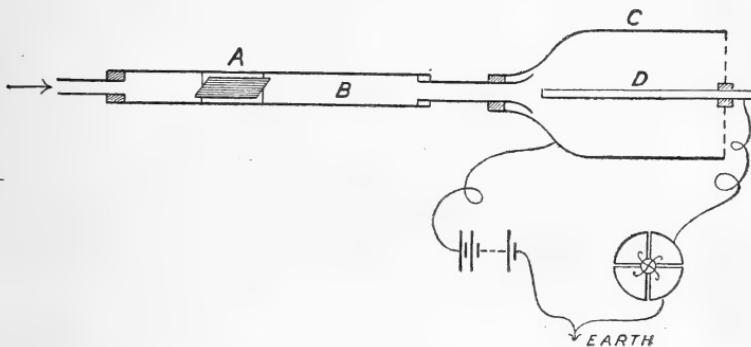
The explanation of the action of slight currents of air is clear on the "emanation" theory. Since the radio-active particles are not affected by an electrical field, extremely minute motions of air, if continuous, remove many of the radio-active centres from between the plates. It will be shown shortly that the emanation continues to ionize the gas in its neighbourhood for several minutes, so that the removal of the particles from between the plates diminishes the rate of discharge between the plates.

#### *Duration of the Radio-activity of the Emanation.*

The emanation gradually loses its radio-active power. The following method was adopted to determine the rate of decay of the intensity of the radiation of the radio-active particles emitted by thorium oxide.

A thick layer of thorium oxide was enclosed in a narrow rectangular paper vessel A (fig. 1), made up of two thicknesses of foolscap-paper. The paper cut off the regular radiation almost entirely, but allowed the emanation to pass through. The thorium thus enclosed was placed inside a

Fig. 1.



long metal tube B. One end of the tube was connected to a large insulated cylindrical vessel C, which had a number of small holes in the end for the passage of air. Inside C was fixed an insulated electrode, D, connected with one pair of quadrants of a Thomson electrometer. The cylinder, C, was connected to one terminal of a battery of 100 volts, the other terminal of which was connected to earth.

A slow current of air from an aspirator or gasometer, which had been freed from dust by its passage through a plug of cotton-wool, was passed through the apparatus. The current of air, in its passage by the thorium oxide, carried away the radio-active particles with it, and these were gradually conveyed into the large cylinder C. The electrometer-needle showed no sign of movement until the radio-active particles were carried into C. In consequence of the ionization of the gas in the cylinder by the radio-active particles, a current passed between the electrodes C and D. The value of the current was the same whether C was connected with the positive or negative pole of the battery. When the current of air had been flowing for some minutes, the current between C and D reached a constant value. The flow of air was then stopped, and the rate of leak between C and D observed at regular intervals. It was found that the current between C and D persisted for over ten minutes.

The following is a series of observations.

TABLE III.  
Potential-difference 100 volts.

Time in Seconds.	Current.
0	1
28	.69
62	.51
118	.23
155	.14
210	.067
272	.041
360	.018

Fig. 2.

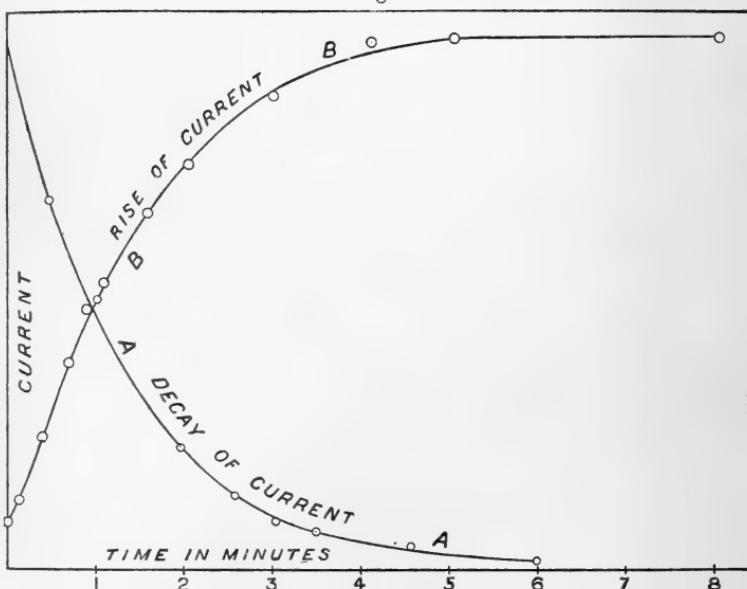


Fig. 2, curve A, shows the relation existing between the current through the gas and the time. The current, just before the flow of air is stopped, is taken as unity. It will be observed that the current through the gas diminishes in a geometrical progression with the time. It can easily be shown,

by the theory of ionization, that the current through the gas is proportional to the intensity of the radiation emitted by the radio-active particles. We therefore see that the intensity of the radiation given out by the radio-active particles falls off in a geometrical progression with the time. The result shows that the intensity of the radiation has fallen to one-half its value after an interval of about *one minute*. The rate of leak due to the emanation was too small for measurement after an interval of ten minutes.

If the ionized gas had been produced from a uranium compound, the duration of the conductivity, for voltages such as were used, would only have been a fraction of a second.

The rate of decay of intensity is independent of the electromotive force acting on the gas. This shows that the radio-active particles are not destroyed by the electric field. The current through the gas at any particular instant, after stoppage of the flow of air, was found to be the same whether the electromotive force had been acting the whole time or just applied for the time of the test.

The current through the gas in the cylinder depends on the electromotive force in the same way as the current through a gas made conducting by Röntgen rays. The current at first increases nearly in proportion to the electromotive force, but soon reaches an approximate "saturation" value.

The duration of the radio-activity was also tested by another method. The paper vessel containing the thorium oxide was placed inside a long brass cylinder over 200 cms. in length. A slow current of air (with a velocity of about 2 cms. per second along the tube) was passed over the thorium oxide along the tube, and then between two insulated concentric cylinders. The rate of leak between the two concentric cylinders (potential-difference 270 volts) was observed when the air had been passing sufficiently long to produce a steady state. The rates of leak were observed for varying positions of the thorium oxide along the tube. Knowing the velocity of the current of air along the tube, the time taken to carry the radio-active particles to the testing-apparatus could be determined. In this way it was found that the rate of decay was about the same as determined by the first method, *i. e.*, the intensity fell to half its value in about one minute.

In this apparatus experiments were also tried to see whether the radio-active particles moved in an electric field. The experiments on the effect of a current of air on the rate of discharge naturally suggest that possibly one of the ions was so large that it moved extremely slowly even in strong electric fields. The results obtained showed that the particles did not move

with a greater velocity than  $\frac{1}{100,000}$  cm. per second for a potential-gradient of one volt per cm.; and it is probable that the particles do not move at all in an electric field. By blowing the emanation into an inductor, no evidence of any charge in the emanation could be detected. We may therefore conclude that the emanation is uncharged, and is not appreciably affected by an electric field.

### *Properties of the Emanation.*

The emanation passes through a plug of cotton-wool without any loss of its radio-active powers. It is also unaffected by bubbling through hot or cold water, weak or strong sulphuric acid. In this respect it acts like an ordinary gas. An ion, on the other hand, is not able to pass through a plug of cotton-wool, or to bubble through water, without losing its charge.

The emanation is similar to uranium in its photographic and electrical actions. It can ionize the gas in its neighbourhood, and can affect a photographic plate in the dark after several days' exposure. Russell\* has shown that the active agent in producing photographic action in the case of metals, paper, &c., is due to hydrogen peroxide. Hydrogen peroxide apparently has the power of passing in some way through considerable thicknesses of special substances, and in this respect the emanation resembles it. Hydrogen peroxide, however, does not ionize the gas in its neighbourhood. The action of hydrogen peroxide on the photographic plate is purely a chemical one; but it is the radiation from the emanation, and not the emanation itself, that produces ionizing and photographic actions.

The radio-active emanation passes through all metals if sufficiently thin. In order to make certain that the emanation passed through the material to be examined and did not diffuse round the edges, the radio-active substance was placed in a square groove of a thick lead plate. Two layers of paper were pasted tightly over the opening to cut off the regular radiation. The material to be tested was then firmly waxed down on the lead plate.

The following numbers illustrate the effect of different metals. The rate of discharge, due to the emanation between two parallel plates 4 cms. apart, was observed.

\* Proc. Roy. Soc. 1897.

Aluminium Foil, thickness = .0008 cm.

Number of Layers.	Rate of Discharge.
0	1
1	.66
3	.42
6	.16

Cardboard, thickness .08 cm.

Layers.	Rate of Discharge.
0	1
1	.40
2	.21

The emanation passed readily through several thicknesses of gold- and silver-leaf. A plate of mica, thickness .006 cm., was completely impervious to the emanation.

When a thick layer of thorium oxide, covered over with several thicknesses of paper, is placed inside a closed vessel, the rate of discharge due to the emanation is small at first, but gradually increases, until after a few minutes a steady state is reached.

These results are to be expected, for the emanation can only slowly diffuse through the paper and the surrounding air. A steady state is reached when the rate of loss of intensity due to the gradual decay of the radio-activity of the emanation is recompensed by the number of new radio-active centres supplied from the thorium compound.

Let  $n$  = number of ions produced per second by the radioactive particles between the plates.

Let  $q$  = number of ions supplied per second by the emanation diffusing from the thorium.

The rate of variation of the number of ions at any time  $t$  is given by

$$\frac{dn}{dt} = q - \lambda n,$$

where  $\lambda$  is a constant.

The results given in Table III. show that the rate of diminution of the number of ions is proportional to the number present.

Solving the equation, it is seen that

$$\log_e (q - \lambda n) = -\lambda t + A,$$

where  $A$  is a constant.

When  $t=0$ ,  $n=0$ ;

therefore  $A = \log_e q$ .

Thus

$$n = \frac{q}{\lambda} (1 - e^{-\lambda t}).$$

With a large potential-difference between the test-plates the current  $i$  through the gas at any time is given by

$$i = ne,$$

where  $e$  is the charge on an ion.

When a steady state is reached,  $\frac{dn}{dt} = 0$ ; and the maximum number  $N$  of ions produced per second by the radio-active particles between the plates is given by

$$N = \frac{q}{\lambda},$$

and the maximum current  $I$  is given by

$$I = Ne.$$

Therefore

$$\frac{i}{I} = 1 - e^{-\lambda t}.$$

The current thus increases according to the same law as a current of electricity rises in a circuit of constant inductance.

This result is confirmed by an experiment on the rise of the current between two concentric cylinders. The thorium oxide enclosed in paper was placed inside the cylinder. A current of air was sent between the cylinders in order to remove the emanation as rapidly as it was formed. The current of air was then stopped and the current between the two cylinders observed, by means of an electrometer, for successive intervals after the current of air ceased. Table IV, gives the results obtained.

TABLE IV.

Length of cylinder = 30 cms.

Internal diameter outer cylinder = 5.5 cms.

External „ inner „ = .8 cm.

100 volts between cylinders.

Time in Seconds.	Current in Scale-divisions per second.
0	2.4
7.5	3.3
23	6.5
40	10.0
53	12.5
67	13.8
96	17.1
125	19.4
184	22.7
244	25.3
304	25.6
484	25.6

The results are expressed in fig. 2, curve B, where the ordinate represents current and the abscissa time. It will be observed that the curve of rise of the current is similar in form to the rise of an electric current in a circuit of constant inductance. The current reaches half its value about one minute after the current of air has stopped,—a result which agrees with the equation given, for  $e^{-\lambda t} = \frac{1}{2}$  when  $t = 60$  seconds (see Table IV.). At the instant of stopping the current of air the current has a definite value, since most of the ions given off by the emanation, before it is blown out of the cylinders, reach the electrodes.

When the source of the emanation is removed,  $q=0$ , and the decay of the number of ions produced by the emanation is given by the equation

$$\frac{dn}{dt} = -\lambda n.$$

If  $n=N$  when  $t=0$ , it is easily seen that

$$\frac{n}{N} = e^{-\lambda t},$$

or

$$\frac{i}{I} = e^{-\lambda t};$$

i. e., the current through the gas diminishes in a geometrical progression. After 20 minutes the current through the gas is only about one millionth part of its initial value.

It has been shown that  $e^{-\lambda t} = \frac{1}{2}$  when  $t = 60$  seconds.

Therefore  $\lambda = \frac{1}{86}$ ,

and

$$N = \frac{q}{\lambda} = 86 q;$$

or the total number of ions produced per second when a steady state is reached is 86 times the number of ions supplied per second by the emanation.

The amount of emanation from thorium oxide increases with the thickness of the layer. When 1 gramme of thorium oxide was spread over a surface of 25 cms., the amount of discharge due to the ordinary radiation had practically reached a maximum. The rate of leak due to the emanation for the same thickness was small. With 9 grammes of oxide spread over the same area, the rate of leak due to the emanation had reached about half its maximum value, which for that case corresponded to four times the rate of leak caused by the ordinary radiation. The emanation thus still preserves its radio-active properties after diffusing through several millimetres of thorium compound.

The emanation is given out whatever the gas by which the thorium is surrounded. The action is very similar whether air, oxygen, hydrogen, or carbonic acid is used.

The rate of discharge due to the emanation diminishes with lowering of the pressure of the air surrounding it. Only a few observations have been made, but the results seem to point to a uniform rate of emission of the emanation at all pressures; but since the intensity of the ionization of the gas varies directly as the pressure, the rate of leak decreases with lowering of the pressure.

The amount of the emanation, so far as the experiments have gone, is also independent of the quantity of water-vapour present.

The power of emitting radio-active particles is not possessed to any appreciable extent by other radio-active substances besides thorium. All the compounds of thorium examined possess it to a marked degree, and it is especially large in the oxide. Two different specimens of the oxide have been used, one obtained from Schuchart of Germany, and the

other from Eimer & Amend of New York. The oxide is prepared by the latter by igniting thorium nitrate obtained from monazite sand.

The amount of discharge caused by the emanation is increased several times by the conversion of the nitrate into the oxide ; but at the same time, the rate of discharge due to the ordinary radiation emitted by the thorium is increased in about an equal ratio. The conversion of the nitrate into the oxide took place below a red heat. On heating in a muffle for some time at white heat, the amount of emanation continually diminished, till after four hours' exposure to the heat, the rate of discharge due to the emanation was only  $\frac{1}{20}$  of the value immediately after its conversion into oxide.

Both thorium oxalate and sulphate act in a similar manner to the nitrate ; but the emanation is still given off to a considerable extent after continued heating.

In considering the question of the origin and nature of the emanation, two possible explanations naturally suggest themselves, viz. :—

(1) That the emanation may be due to fine dust particles of the radio-active substance emitted by the thorium compounds.

(2) That the emanation may be a vapour given off from thorium compounds.

The fact that the emanation can pass through metals and large thicknesses of paper and through plugs of cotton-wool, is strong evidence against the dust hypothesis. Special experiments, however, were tried to settle the question. The experiments of Aitken and Wilson \* have shown that ordinary air can be completely freed from dust particles by repeated small expansions of the air over a water-surface. The dust particles act as nuclei for the formation of small drops, and are removed from the gas by the action of gravity.

The experiment was repeated with thorium oxide present in the vessel. The oxide was enclosed in a paper cylinder, which allowed the emanation to pass through it. After repeated expansions no cloud was formed, showing that for the expansions used the particles of the emanation were too small to become centres of condensation of the water-vapour. We may therefore conclude, from this experiment, that the emanation does not consist of dust particles of thorium oxide.

It would be of interest to examine the behaviour of the emanation for greater and more sudden expansions, after the

\* Trans. Roy. Soc. 1897.

manner employed by C. T. R. Wilson\* in his experiments on the action of ions as centres of condensation.

The emanation may possibly be a vapour of thorium. There is reason to believe that all metals and substances give off vapour to some degree. If the radio-active power of thorium is possessed by the molecules of the substance, it would be expected that the vapour of the substance would be itself radio-active for a short time, but the radio-active power would diminish in consequence of the rapid radiation of energy. Some information on this point could probably be obtained by observation of the rate of diffusion of the emanation into gases. It is hoped that experimental data of this kind will lead to an approximate determination of the molecular weight of the emanation.

Experiments have been tried to see if the amount of the emanation from thorium oxide is sufficient to appreciably alter the pressure of the gas in an exhausted tube. The oxide was placed in a bulb connected with a Plücker spectroscopic tube. The whole was exhausted, and the pressure noted by a McLeod gauge. The bulb of thorium oxide was disconnected from the main tube by means of a stopcock. The Plücker tube was refilled and exhausted again to the same pressure. On connecting the two tubes together again, no appreciable difference in the pressure or in the appearance of the discharge from an induction-coil was observed. The spectrum of the gas was unchanged.

Experiments, which are still in progress, show that the emanation possesses a very remarkable property. I have found that the positive ion produced in a gas by the emanation possesses the power of producing radio-activity in all substances on which it falls. This power of giving forth a radiation lasts for several days. The radiation is of a more penetrating character than that given out by thorium or uranium. The emanation from thorium compounds thus has properties which the thorium itself does not possess. A more complete account of the results obtained is reserved for a later communication.

McGill University, Montreal,  
September 13th, 1899.

\* Phil. Trans. Roy. Soc. vol. clxxxix. (1897).

II. *On the Thermal Conductivity of Vulcanite.*  
By B. OSGOOD PEIRCE \*.

LAST year Dr. R. W. Willson and I published in the ‘Proceedings of the American Academy of Arts and Sciences’ an account of some determinations of the thermal conductivities of different kinds of marble, made by the so-called “Wall Method”†. The horizontal bases of a rectangular prism, of height small compared with the area of a horizontal cross section, were kept for a long time at constant temperatures, the final temperatures at two or more points in the vertical axis were determined, and the flux of heat through a definite central portion of the colder base was measured.

In each experiment of one of our sets a rectangular prism 60 centim. square and not more than 6 centim. high was built up of a slab of the material to be tested, enclosed between two other slabs of the same material. Between each two consecutive slabs of the prism was placed a thin metal sheet. This consisted of two rectangular leaves of tinfoil, about 60 centim. long and a little less than 30 centim. wide, placed side by side and separated by a narrow ribbon thermal element made by butt-jointing, end to end, with the help of silver solder, a strip of german-silver and a strip of copper of the same thickness as the tinfoil. After the edges of the ribbon had been varnished so as to prevent electrical contact, the ribbon and the tinfoil could be placed close together so as to form a continuous sheet of metal 60 centim. square and about  $\frac{1}{10}$  of a millimetre thick.

\* Communicated by the Author.

† Despretz, *Ann. de Chimie et de Physique*, 1827. Péclat, *Ann. de Chimie et de Physique*, 1841. Tyndall, *Phil. Mag.* 1853. Hopkins, *Phil. Trans.* 1857. Pfäff, *Pogg. Ann.* cxiii. 1861. J. D. Forbes, *Proc. Edin. Soc.* iv. Ångström, *Pogg. Ann.* cxiv. 1861. Neumann, *Ann. de Chimie et de Physique*, 1862. G. Forbes, *Proc. Edin. Soc.* viii. 1873. Herschel, Lebourg, and Dunn, *Rep. Brit. Assoc.* 1873. v. Beetz, *Pogg. Ann.*, Jubelband, 1874. Smith and Knott, *Proc. Edin. Soc.* 1875. Lodge, *Phil. Mag.* 1878. Less, *Journ. de Phys.* vii. 1878. Ayrton and Perry, *Phil. Mag.* 1878. H. F. Weber, *Vierteljahrsschrift d. Züricher Naturf. Ges.* 1879. Thoulet, *Comptes Rendus*, 1882. Lagarde, *Comptes Rendus*, 1882. v. Littrow, *Wien. Ber.* lxxi. Stefan, *Carl's Rep.* xiii. Jannettaz, *Comptes Rendus*, 1884. Tuchschnid, *Beiblätter z. Wied. Ann.* 1884. M. Ballo, Dingler's *Journ.* 1886. H. Meyer, *Wied. Ann.* 1888. K. Jamagawa, *Beiblätter z. Wied. Ann.* 1889. G. Stadler, *Inaug. Diss.*, Berne, 1889. Venske, *Göttinger Nachrichten*, 1891. Grassi, *Atti Ist. Napoli*, 1892. Lees, *Phil. Trans.* 1892. R. Weber, *Bull. Soc. Science Nat. Neuch.* 1895. Lord Kelvin and Mr. Murray, *Proc. Royal Soc.* 1895. Peirce and Willson, *American Journal of Science*, 1895. Lees and Chorlton, *Phil. Mag.* 1896. Oddone, *Rend. R. Accad. d. Lincei*, 1897. W. Voigt, *Wied. Ann.* 1898. Lees, *Proc. Royal Society*, 1898.

It is evident that when one end of a regular right prism of  $2n$  sides made of homogeneous material is kept at a constant temperature  $V_0$ , and the other end at a constant temperature  $V_t$ , while its other faces are kept as nearly as possible at some constant temperature between  $V_0$  and  $V_t$ , the temperatures on the axis of the prism in its final state depend very largely on the ratio of the length of the axis of the prism to that of a diagonal of a cross section ; and that, if this ratio be small enough, the temperature conditions to which the sides are subjected are of slight importance. The temperatures at points on the axis of a relatively thin disk, one face of which is kept at  $0^\circ$  C. and the other at  $100^\circ$  C., are not measurably different, whether the curved surface is kept at  $0^\circ$  C. or  $100^\circ$  C., from the temperatures at corresponding points on the axis of an infinite disk of the same thickness, the faces of which are kept at  $0^\circ$  C. and  $100^\circ$  C. respectively.

It is easy to see, moreover, that in the case of a prism or cylinder of poorly conducting material, the bases of which are kept at constant temperatures while its side faces are exposed to variations of temperature, the introduction of such metal sheets as we have sometimes used certainly affects to some slight degree the temperatures in the rest of the prism.

Since it was extremely difficult to control the temperatures on the side faces of our prisms, it was necessary to make sure that the dimensions of the prisms were such that probable temperature changes at these faces could not sensibly influence temperatures at points near the axis. We were able to get some useful information, to be checked afterwards by experiment, from a discussion of the solutions (obtained on the very approximate supposition that the thermal conductivities of our materials did not change with the temperature) of the two simple problems in heat-conduction which follow.

(1) The radius of the base of a homogeneous right cylinder of revolution of length  $l$  is  $a$ . If in the final state the temperature  $V$  (which is harmonic within the cylinder) has a constant value  $V_0$  on one (the lower) base, the constant value  $V_t$  on the upper base, and the constant value  $\bar{V}$  on the convex surface ; and if the axis of the cylinder be used as axis of  $z$ , with origin at the centre of the lower base,  $V$  is given by the equation

$$V = \bar{V} + 2 \sum_{p=1}^{p=\infty} \frac{J_0\left(\frac{x_p r}{a}\right) \left\{ (V_0 - \bar{V}) \sinh\left(\frac{x_p(l-z)}{a}\right) + (V_t - \bar{V}) \sinh\left(\frac{x_p z}{a}\right) \right\}}{x_p \cdot J_1(x_p) \cdot \sinh\left(\frac{x_p l}{a}\right)},$$

where  $J_0$  and  $J_1$  represent Bessel's Functions of the zeroth and first order respectively, and  $x_p$  is the  $p$ th root in order of magnitude of the equation  $J_0(x)=0$ .

If

$$T_{r,z} \equiv \sum_{p=0}^{\infty} \frac{J_0\left(\frac{x_p r}{a}\right) \cdot \sinh\left(\frac{x_p z}{a}\right)}{x_p \cdot J_1(x_p) \cdot \sinh\left(\frac{x_p l}{a}\right)},$$

it follows that

$$V = \bar{V}(1 - 2T_{r,z} - 2T_{r,l-z}) + 2V_l T_{r,z} + 2V_0 T_{r,l-z};$$

and if, moreover,

$$\bar{V} = V_l = 0, \text{ then } V = 2V_0 T_{r,l-z}.$$

By using ten-place logarithms and, in some instances, more than sixty terms, we computed the numerical values of the series  $T_{r,z}$  for about thirty different values of  $r$ ,  $z$ , and  $a/l$ . We found, for instance, that if  $a$  is as great as  $5l$  and if  $r$  is not greater than  $l$ ,  $T_{r,z}$  does not, for any value of  $z$ , differ from the corresponding value for the same  $r$  and  $z$  when  $a$  is infinite, earlier than in the fifth decimal place; and that, keeping four decimal places, we may write in this case

$z$ .	$T_{r,z}$ .
0	0·0000
$\frac{1}{4}l$	0·1250
$\frac{1}{2}l$	0·2500
$\frac{3}{4}l$	0·3750
$l$	0·5000

The following table gives values of  $T_{r,z}$  at points on the axis of the cylinder (where  $r=0$ ) for various values of  $a/l$ .

	$z=0$ .	$z=\frac{1}{4}l$ .	$z=\frac{1}{2}l$ .	$z=\frac{3}{4}l$ .	$z=l$ .
$a=\frac{1}{4}l$ .....	0	0·0006	0·0065	0·0703	0·5
$a=\frac{1}{2}l$ .....	0	0·0196	0·0697	0·2116	0·5
$a=\frac{3}{4}l$ .....	0	0·0558	0·1427	0·2908	0·5
$a=l$ .....	0	0·0857	0·1920	0·3320	0·5
$a=\frac{5}{4}l$ .....	0	0·1144	0·2349	0·3642	0·5
$a=2l$ .....	0	0·1224	0·2464	0·3724	0·5
$a=3l$ .....	0	0·1249	0·2498	0·3748	0·5
$a=5l$ .....	0	0·1250	0·2500	0·3750	0·5

We inferred from these results that if the faces of a homogeneous disk, the radius of which is at least five times as great as its thickness, be kept at temperatures of  $100^{\circ}$  C. and  $0^{\circ}$  C. respectively, the temperature in the final state, at every point within a distance from the axis equal to the thickness of the disk, would be the same within about one hundredth of a degree, whether the curved surface were kept at  $0^{\circ}$  or at  $100^{\circ}$ . Since in practice there is a gradual fall of temperature at the curved surface of such a disk from  $100^{\circ}$  to  $0^{\circ}$  in passing from the hot to the cold side, the approximation is really much closer than  $0^{\circ}01$ ; and it is evident that, for the purposes of the present problem, a disk of such relative dimensions, if we consider only the points near the axis, has practically an infinite radius and the isothermal surfaces in this portion of the disk are sensibly plane.

(2) The radius of the base of a right cylinder of revolution of height  $l$  is  $a$ . The centre of the lower base is used as the origin of a system of columnar coordinates  $(r, \theta, z)$ , the axis of the cylinder being the axis of  $z$ . The temperature,  $V$ , continuous everywhere within the cylinder, has the value zero on the curved surface and on the lower base, and the constant value  $V_1$  on the upper base. The planes  $z=l'$ ,  $z=l''$  divide the cylinder into three portions (1), (2), and (3), in which  $V$  is represented analytically by three harmonic functions,  $V_1$ ,  $V_2$ ,  $V_3$ , respectively. The thermal conductivities of the three portions of the cylinder are  $k_1$ ,  $k_2$ ,  $k_3$  respectively. If, when  $z=l'$ ,

$$k_1 \frac{\partial V_1}{\partial z} = k_2 \frac{\partial V_2}{\partial z},$$

$$\text{and when } z=l'', \quad k_2 \frac{\partial V}{\partial z} = k_3 \frac{\partial V_3}{\partial z},$$

then

$$V_1 \equiv \sum_{p=0}^{p=\infty} A_1 \cdot J_0\left(\frac{x_p r}{a}\right) \cdot \sinh\left(\frac{x_p z}{a}\right),$$

$$V_2 \equiv \sum_{p=0}^{p=\infty} J_0\left(\frac{x_p r}{a}\right) \left[ A_2 \sinh\left(\frac{x_p z}{a}\right) + B_2 \cosh\left(\frac{x_p z}{a}\right) \right],$$

$$V_3 \equiv \sum_{p=0}^{p=\infty} J_0\left(\frac{x_p r}{a}\right) \left[ A_3 \sinh\left(\frac{x_p z}{a}\right) + B_3 \cosh\left(\frac{x_p z}{a}\right) \right],$$

where  $A_1$ ,  $A_2$ ,  $A_3$ ,  $B_2$ , and  $B_3$  are subject to the conditions

$$A_1 \sinh\left(\frac{x_p l'}{a}\right) = A_2 \sinh\left(\frac{x_p l'}{a}\right) + B_2 \cosh\left(\frac{x_p l'}{a}\right),$$

$$k_1 A_1 \cosh\left(\frac{x_p l'}{a}\right) = k_2 \left[ A_2 \cosh\left(\frac{x_p l''}{a}\right) + B_2 \sinh\left(\frac{x_p l'}{a}\right) \right],$$

$$A_2 \sinh\left(\frac{x_p l''}{a}\right) + B_2 \cosh\left(\frac{x_p l''}{a}\right) = A_3 \sinh\left(\frac{x_p l''}{a}\right) + B_3 \cosh\left(\frac{x_p l''}{a}\right).$$

$$k_2 \left[ A_2 \cosh\left(\frac{x_p l''}{a}\right) + B_2 \sinh\left(\frac{x_p l''}{a}\right) \right] \\ = k_3 \left[ A_3 \cosh\left(\frac{x_p l''}{a}\right) + B_3 \sinh\left(\frac{x_p l''}{a}\right) \right],$$

$$A_3 \sinh\left(\frac{x_p l}{a}\right) + B_3 \cosh\left(\frac{x_p l}{a}\right) = \frac{2V_l}{x_p J_1(x_p)},$$

and where  $x_p$  is the  $p$ th root in order of magnitude of the Bessel's equation  $J_0(x)=0$ .

If, for brevity, we denote the quantities

$$\sinh\left(\frac{x_p \cdot l}{a}\right), \quad \cosh\left(\frac{x_p \cdot l}{a}\right), \quad \sinh\left(\frac{x_p \cdot l'}{a}\right), \quad \cosh\left(\frac{x_p \cdot l'}{a}\right), \\ \sinh\left(\frac{x_p \cdot l''}{a}\right), \quad \cosh\left(\frac{x_p \cdot l''}{a}\right), \quad \frac{2V_l}{x_p \cdot J_1(x_p)},$$

by  $s, c, s', c', s'', c'',$  and  $\Omega$ , respectively,

$$A_1 =$$

$$-k_2 k_3 c \Omega \\ e' s' (k_1 - k_2) \{ k_2 c s'' (s c'' - c s'') + k_3 c c'' (c c'' - s s'') \} + (k_1 c'^2 - k_2 s'^2) \{ c s'' k_3 (s s'' - c c'') + k_2 c c'' (s'' c - s c'') \}$$

If in the special case where  $k_1$  and  $k_3$  are equal, we write  $k_1 = \mu k_2 = k_3$ , we get

$$A_1 =$$

$$-\mu \Omega$$

$$e' s' (\mu - 1) \{ s'' (s c'' - c s'') + \mu c'' (c c'' - s s'') \} + (\mu c'^2 - s'^2) \{ \mu s'' (s s'' - c c'') + c'' (s'' c - s c'') \},$$

with corresponding values for the other coefficients.

Similar results can easily be obtained for a case where the cylinder is supposed to be built up of more than three disks.

By the use of these equations it is possible to determine how much the presence of a thin disk of metal between two disks of some poorly conducting material affects temperatures near the axis of the cylinder under different temperature conditions at the curved surface of the cylinder. We inferred from our computation, which involved a great deal of labour, that with probable temperature conditions in the side faces of a prism of the dimensions we generally use, the thermal elements do not sensibly distort the isothermal surfaces within

a distance from the axis equal to the thickness of the prism. This inference was justified by the results of our experiments.

In some of our work we used, instead of the ribbon thermal elements with tinfoil "wings" described above, fine wire thermal junctions inserted in shallow grooves accurately cut to a given depth in the faces of the slabs to be tested. These grooves were made in a Brown and Sharpe Universal Milling Machine by extremely thin hard steel saws (No. 34 B. & S. Gauge) held between flat disks of somewhat smaller diameters than the saws to prevent buckling. The wire that we used fitted the grooves very closely, and we hoped that the indications of the thermal couples would enable us to determine the mean temperature of the walls of the groove when the grooved slab was placed against a flat one. We found, however, that the results were often most irregular; and although we spent some time in attempts to make observations obtained in this way trustworthy, we met with little success. Sometimes our results were good, and sometimes considerably in error.

The ribbon thermal elements gave consistent results at all times, provided that the junctions themselves were in contact with the slabs between which they lay. If the tinfoil wings were considerably thicker than the junction-ribbon, or if the junction itself were scraped thin, the reading might be in error by an amount not easy to be accounted for by the mere resistance of the thin air-film on each side of the junction. We shall wish to discuss this matter at some length in the near future in the light of some of our observations.

It is obvious that in the case of such material as glass, the use of fine wire thermal elements in the manner just described is practically impossible, and that the specific resistance of such metal leaves as we use was in every case hundreds of times less than that of the slabs between which they were placed. The question of contact-resistance (*Uebergangswiderstand*) will be discussed later on. In some experiments we used wire thermopiles inserted in a thin metal disk: we had also at command a prism-holder so constructed that the fine wire elements could be immersed in very thin layers of mercury.

The present paper gives an account of a series of measurements of the thermal conductivities of different specimens of "hard rubber" or "vulcanite." These determinations were made, for the most part, with the help of apparatus previously used by Dr. Willson and myself. That the method may be understood, it will be necessary to describe this apparatus somewhat at length.

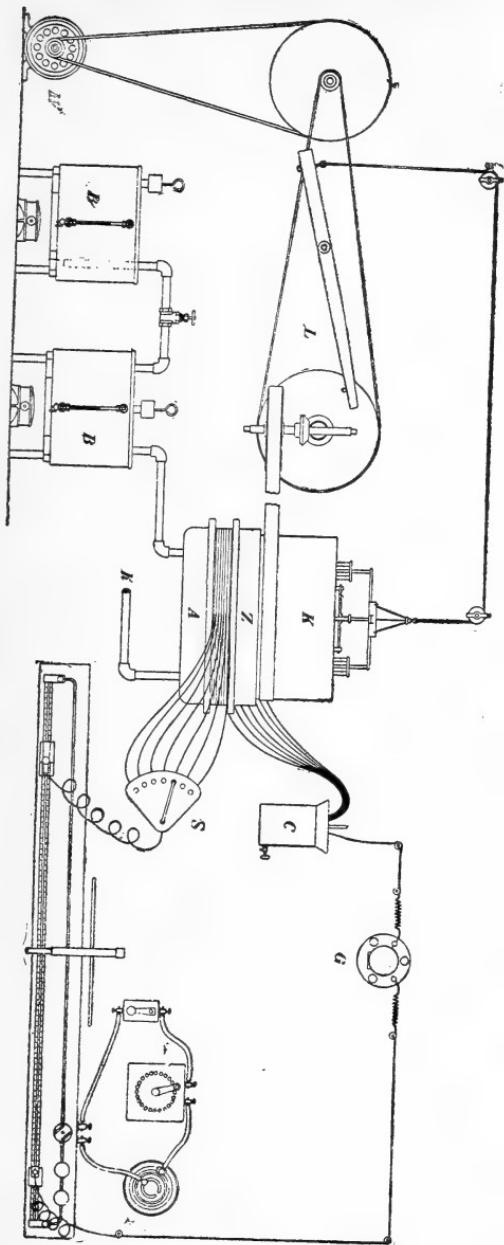


Fig. 1.

Fig. 1 represents, without any of its elaborate system of jackets, the apparatus which we used in determining the absolute conductivities, between  $0^{\circ}$  C. and  $100^{\circ}$  C., of various substances.

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A represents the hot chamber, weighing about two hundred kilograms, which rests in a thick jacket on a heavy table or stand made to hold it. A is connected directly with one (B) of two stout-walled copper boilers, B and B', each of which holds about 40 litres of water. A light cup-shaped weight, inverted and laid on a large tube with squared end which projects above the top of the boiler, acts as a sensitive safety-valve and prevents any appreciable rise in temperature within the boiler. B can be refilled when necessary with boiling water from B' without stopping the constant flow of steam through A, by means of the siphon f which is provided with a valve. The steam, after passing through the hot chamber, is led to the outer air by a jacketed pipe h descending from the bottom of A.

The connexions of the thermal elements are led out of the sides of the prism shut in by A and Z, and are held between slabs of wood, which act as a sort of guard-ring jacket to the prism for about 40 centim. before they emerge. The platinoid or german-silver leads of these thermal junctions within the prism are soldered together, and to a copper wire leading to the (copper) wire of a potentiometer. The copper ends of the couples lead to a mercury-switch by which any one of them, or any pair pitted against other, may be quickly connected with the potentiometer. On its way from the switch to the cold junctions in C through the potentiometer-wire the current encounters only copper. By means of a somewhat elaborate standard potentiometer, not shown in the diagram, the resistance, R, in the potentiometer-circuit can be so adjusted that every millimetre on the potentiometer-wire corresponds to any desired small potential-difference, such as one microvolt or one-tenth of a microvolt. Rather than make this adjustment many times a day to conform to the varying temperature of the copper wire, however, we found it better to determine the slight corrections necessary to reduce the readings to absolute measure, by noting at frequent intervals the indications of a standard thermal couple, the electromotive force of which is well known. The potentiometer-wire, which is 0.25 millim. in diameter, can be changed in a few seconds for a new wire, if the old should become dented or stretched. An iron casting, Z, seen in plan in fig. 3 and in elevation in fig. 2, accurately planed below and turned true above, is the bottom of the box. Between this casting (which can be bolted to A) and A is held the prism to be experimented on. While Z was in the lathe a small hole, H, about 3 millim. in diameter and 4 millim. deep, was drilled exactly in the centre of its upper face. Subsequently

a piece of solid drawn brass tube 12·3 centim. in outside diameter and 13·5 centim. high, with carefully squared ends, was held centrally in Z by means of a wooden disk turned to fit it, and a central pin inserted in H, and was then soldered firmly to Z. This was accomplished, after many trials of other materials, by the use of white pitch as a flux; and the result left nothing to be desired. The walls of the pot thus formed were jacketed on the outside, except for a height of

Fig. 2.

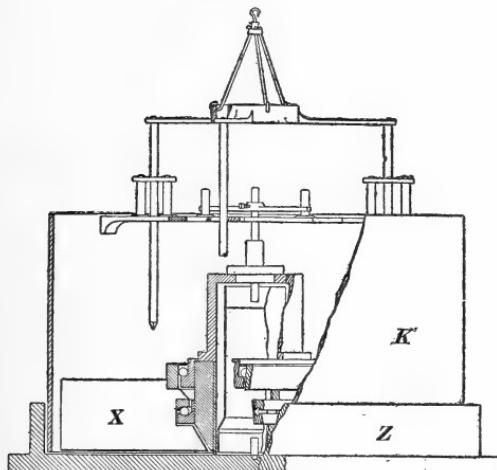
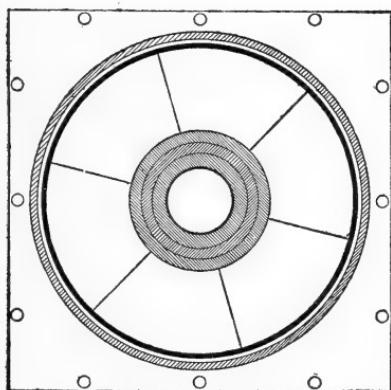


Fig. 3.



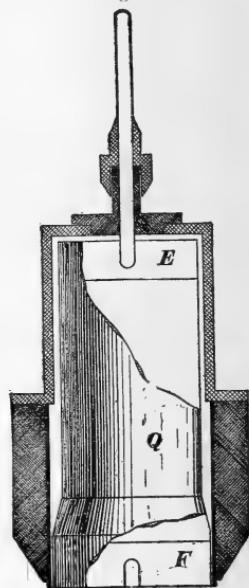
about 2 millim. at the bottom, by an inch-thick casting of hard rubber made for the purpose in the form of a cylindrical shell. This casting, which was cut off square at the top of

the pot, tapered to nothing near the bottom, but did not rest upon the floor (fig. 4). Upon the top of this jacket was fastened a hard rubber cover shaped somewhat like a cylindrical hat. This had an opening at the top which could be closed by an accurately fitting rubber plug. In the box, P, thus made, is placed a thin-walled ice-holder, Q, open at top and bottom, of the same outside diameter below as the inside of the brass pot, but somewhat smaller above, so as to leave an air-space between it and the walls of the pot.

In order that the holder may be easily rotated, a pin soldered to a thin diametral web, F, which runs across the bottom of the holder, is inserted in H, and a vertical brass rod soldered to a similar web, E, at the top of the holder passes through a hole in the cover of the pot which it fits closely. A hard rubber thimble fitting tightly on the rod and turning with it permits the slow entrance of cold air into the pot without allowing any water to leak in. The rod can be clamped at pleasure to a brass yoke which is turned by the motor. In order to prevent the introduction of heat into the pot by conduction down the rod, the exposed portion is buried in cracked ice held in a thin metallic cup carried by the yoke and resting on it. When the holder is filled with ice and is turned by the motor, the web at the bottom compels the ice to rub over the floor of the casting, since the holder itself has no bottom; and as a result of this, the lower surface of the ice quickly acquires and keeps a mirror-like surface. The drip from the pot comes out of the edge of the casting Z through a straight hole about 26 centim. long and 0·6 centim. in diameter drilled in the plate and ending just inside the pot. The whole apparatus is very slightly tilted so as to ensure the steady outflow of the drip.

A large cylinder, K, 35 centim. high, made of rolled brass 4 millim. thick, and open at the top and bottom, is mounted on brass ball-bearings placed on the outside of the hard rubber jacket of the pot, P, by means of six vanes, one of which, X, is shown in fig. 2. K weighs about 20 kilograms when empty, and rests upon 144 brass balls each about 12 millim.

Fig. 4.



in diameter. When set in motion by a slight push, it continues to rotate for about a minute before coming to rest. K is so truly hung that the outside can be used as a pulley, and the whole can be rotated by the use of the belt shown in fig. 1. The vanes reach to about 2 millim. of the floor of the box, and when the whole is filled with cracked ice and then rotated, the ice at the bottom which rubs on Z soon gets and holds a very smooth surface. A hole in the bottom of Z carries away the drip and prevents any accumulation of water on the floor of the ice-box. We were at first troubled by irregularities arising from honeycombing of the ice in the ice-box; and to remedy this a suitably loaded brass tripod is used to pack the ice by light blows delivered at intervals of 21 seconds by the aid of the lever L. A train of four wheels is necessary to reduce the speed of K to one revolution in 20 seconds, though only two wheels are shown in the drawings. The tripod slides in guides which revolve with K, and a swivel at the top prevents the cord from twisting.

The rotation of K and of the inside ice-holder, Q, which is connected with K by a thin yoke, are matters of much importance. The continual rubbing of the ice over the flat surface of the casting seems to be necessary, if the latter is to be kept at a uniform constant temperature for hours. The heat produced in rotating Q is so little as to be quite negligible. The ice in K is piled up so as to cover P completely; and we have been unable to detect any difference between the temperatures within and without P by fine, properly protected thermal junctions introduced for the purpose. If, while K revolves, Q is kept still, the amount of ice melted in Q becomes irregular, though the whole amount of drip in two or three hours is not very different from the amount of steady drip in an equal time when Q is rotating. Only selected lumps of ice are put into Q. The ice to be used is first broken up into pieces weighing something like 15 grams each, by means of an ice-cracking machine, and these pieces are then put into ice-water so that their sharp edges may become slightly rounded. They are then drained and dropped into Q. In this way a slight amount of water attached to the ice is introduced into Q; but the error due to this cause appears to be of slight importance. In some experiments the ice to be used was carefully dried in cold blotting-paper; but this precaution does not seem to be necessary, though the use of small bits of ice with sharp edges is to be avoided. Q's capacity is about 2000 cub. centim. After Q has been freshly filled in the course of any experiment while K is rotating, no record is kept for some time, perhaps fifteen minutes, of the amount of

drip. Before the expiration of this interval the extra water introduced into Q with the ice has drained off, and the indications have become steady. After this the apparatus is allowed to run for about two hours until 300 grams of ice, or less, has been melted, and then Q is refilled. The drip-tube always contains a few drops of water, but this amount remains sensibly constant during the progress of one experiment. The drip is collected in a graduated vessel, and the approximate amount is noted from time to time to see whether the flow is steady. The whole is then more accurately determined by weighing, at longer intervals.

The regularity of drip is a far more sensitive test of the approximate attainment of the final state of the body experimented on and its surroundings than is a sensibly constant temperature gradient on the axis. In most experiments with the apparatus just described, a sufficiently steady state has been attained in about seven hours from the beginning of the heating. Sheets of blotting-paper were generally inserted between the prism to be tested and the hot and cold boxes, to serve as elastic pads, and to prevent the possible wetting of the edge of the prism by moisture condensed on the ice-box. The presence of this paper prolonged the time of waiting for the final state to be attained, but did not influence the results of the measurement of the conductivity of the prism. When filled with ice, Z and K weigh about 300 kilograms, and the additional pressure due to the bolts is considerable; so that, when the prism is made up of brittle material like glass, the blotting-paper or an equivalent must be used to prevent the prism from injury. Since hard rubber becomes very soft at temperatures above  $100^{\circ}$  C., it did not seem worth while to test its thermal conductivity at high temperatures; and it is not necessary to give any account here of the apparatus intended for use at temperatures as high as the boiling-point of sulphur.

After the absolute conductivity of a particular specimen has been carefully determined, between various pairs of temperature-limits, in the apparatus just described, the conductivity of any other specimens can be easily obtained in the same apparatus merely by determining the temperature-gradient in the final state on the axis of a prism built up of the slab already tested, and the slab to be examined, with their attendant thermopiles and such other thin slabs as may be conveniently used. By varying the order of the slabs on different occasions, the temperatures at the faces of the slab to be examined can be altered, it being always understood that the thermal elements must be placed between slabs of approxi-

mately the same conductivities. The relative conductivities of different materials, if these conductivities are not widely different, can be determined with great accuracy by this method; and it is possible to use much smaller slabs than are necessary if one is to determine absolute conductivities. I have two smaller pieces of apparatus very like the large one already described, except that neither cold box has a device for determining the amount of heat coming through the prism. One of these is intended for slabs 35 centim. square; the other, made wholly from brass, for disks 20 centim. in diameter. Since it is not easy to get thin plane-faced slabs of some materials 60 centim. square, it is usually best to compare in the small apparatus small disks of such materials with a disk of some standard material cut from a plate previously tested in the larger apparatus.

When one considers the passage of heat through a prism or wall built up of separate slabs, one is led to ask whether the cracks between the slabs do not introduce great irregularities. We know that it is practically impossible so to press together flat slabs of any material that there shall not be a relatively large contact-resistance to the passage of an electrical current across the common surface. Should we not expect the thermal conductivity of a prism made up of two or more slabs of a given material to be different from that of a prism of the same thickness made of a single slab of this material? It was necessary to appeal to experiments for an answer to this question. Fortunately I had considerable quantities of a special kind of plate-glass and of a special brand of hard rubber in which I have been unable to detect any change of thermal conductivity with the temperature between 20° C. and 80° C. All the glass was nearly of the same thickness, but, by fastening a disk of the rubber to the face-plate of a large massive engine-lathe, and using a broad, very sharp tool (kept cool by water) with slow speed, and a very fine cut, it was possible to reduce the thickness of the disk and to keep the faces almost exactly plane. Of these materials I have built up at different times a number of prisms in different ways, and have tested these prisms in my apparatus. In every case the conductivity seemed to be entirely independent of the thickness of the prism and of the number of slabs out of which it was built. It has also appeared that the conductivity of a prism made up of a number of disks was not changed to any measurable amount by introducing thin metallic leaves to separate every slab from its next neighbours. In the cases of some heterogeneous prisms built up of slabs of different substances separated by thermal elements, the results

were not regular; and for this reason I have felt it unwise, as I have already said, to trust the indications of thermal elements which lie between substances of widely different conductivities. Of course it is of great importance that the faces of the slabs should be practically plane.

I had at my disposal fourteen different specimens of hard rubber, thick enough to be used conveniently in my apparatus, and much of this was in sheets about 120 centim. by 50 centim. So much of it as was bought for the purposes of this investigation came from three well-known makers. Besides this new rubber, however, there were a number of pieces from unknown sources, which had been lying in the laboratory for indefinite periods. The specific gravities of the different specimens examined differed slightly from each other, but by not nearly so much as 1 per cent. in the extreme cases. The specific gravity of the rubber used as a standard is about 1.202. The specific heat of the rubber increases with the temperature, as may be inferred from the subjoined Table, in the second column of which is given the number of calories required to raise one gram of a certain specimen of thin sheet rubber from 25° C. to the temperatures given in the first column. The third column gives the average specific heat between 25° C. and these temperatures.

Temperatures.	Calories.	Average Specific Heat.
35	3.17	0.317
45	6.46	0.323
55	9.91	0.330
65	13.47	0.337
75	17.20	0.345
85	21.22	0.354
95	25.48	0.364
100	27.90	0.372

The average specific heat of another specimen of thin rubber between 25° C. and 100° C. was 0.370. That of the thicker standard rubber was 0.339.

Since hard rubber is an extremely poor conductor of heat, a long time was required in the case of any prism for the final state to be reached approximately. After about seven or eight hours, if the temperatures of the hot and cold boxes were kept quite constant, the temperatures at all points on the axis could generally be assumed to be within  $\frac{1}{20}$  of a

degree of their final values; and, in view of the variable composition of what is called "hard rubber," "ebonite," or "vulcanite," in the market, and of the extreme difficulty of keeping the temperature of the hot box constant within less than  $\frac{1}{10}$  of a degree for any great number of hours, it did not seem desirable to extend the experiments further. In what follows the conductivity is given in every case to three decimal figures; but it is evident that the third figure is not quite determined.

*Experiment (a).*—A compound slab, made up of two plates (A and B) of a certain kind of hard rubber which I chose as a standard, was placed between two other pieces of hard rubber to form a prism. Each plate was about 60 centim. long by 50 centim. broad. The average thickness of A was 1.270 centim. and that of B 1.260 centim. In the final state the thermal elements on the warmer side of A, between A and B, and on the cooler side of B, indicated  $74^{\circ}9$ ,  $45^{\circ}2$ , and  $15^{\circ}7$  respectively. The rate of melting of the ice in the box was 102 grams in almost exactly 8760 seconds. Assuming the area of the bottom of the ice-pot to be 126.7 square centim. and the latent heat of melting ice to be 79.25, this corresponds to the conductivity for each slab of 0.000311.

*Experiment (b).*—Plate A with two thermal elements enclosed by two other "guard-sheets" of hard rubber was made into a prism with three plates of glass. In the final state the temperatures of the elements on the faces of A were  $60^{\circ}1$  and  $24^{\circ}9$  respectively. In 11,220 seconds, 154.8 grams of ice were melted. This again corresponds to a conductivity between  $60^{\circ}$  and  $25^{\circ}$  of 0.000311.

Two other experiments, in which the final gradients on the axes of prisms built up of disks about 20 centim. in diameter, made of this rubber, were determined, failed to show any sensible variation of the conductivity with the temperature between  $65^{\circ}$  and  $16^{\circ}$ .

*Experiment (c).*—A compound slab made of A and a plate C (of the same dimensions as A but purporting to come from another maker), with their thermal elements and "guard-plates" of rubber, were used to form a prism for the large apparatus. In the final state the indications of the elements on the warm side of A, between A and C, and on the cool side of C were, respectively,  $69^{\circ}8$ ,  $41^{\circ}1$ , and  $13^{\circ}1$ , so that the conductivity of C between  $41^{\circ}$  and  $13^{\circ}$  appears to be 0.000319.

After this a number of disks 20 centim. in diameter, which seemed alike in their physical properties, were cut from the standard rubber and used with other disks to form prisms for the smaller apparatus.

*Experiments (d) to (o).*—By these standard disks the conductivities of 12 other specimens were easily obtained. I give in the next Table the results, not in the order in which the experiments were performed, but, for convenience, in the order of the conductivities of the specimens.

Specimens.	Thickness in centims.	Temperature Limits.	Conductivity.
D .....	1.584	44.4 and 16.5	0.000317
E .....	1.265	40.1 , 15.8	0.000313
F .....	1.297	40.1 , 14.9	0.000309
G .....	1.254	40.5 , 16.1	0.000307
H .....	0.979	37.0 , 16.4	0.000305
I .....	0.499	50.0 , 23.9	0.000282
J .....	1.003	37.0 , 12.1	0.000256
K .....	0.945	36.1 , 12.6	0.000254
L .....	0.797	35.2 , 12.5	0.000237
M .....	0.643	33.1 , 13.2	0.000217
N .....	0.644	32.8 , 12.2	0.000214
O .....	0.498	30.5 , 12.8	0.000200

In view of the suspicious decrease of the thermal conductivity with the thickness of the piece experimented upon, it is well to say that some manufacturers apparently use rubbers of different compositions for thick and thin plates. Much cheap, thin rubber is to be had in the market, and the specific electrical resistance of some of this is so low as to make the material useless for insulating purposes. Of the specimens mentioned in the table, G and H are pieces of expensive rubber made especially for use in induction-coils of high grade. K, which is nearly of the same thickness as H, is an excellent rubber of high electrical resistance, but is not quite equal in this respect to H, which has a very different thermal conductivity. Extended experimentation seemed to show that the indications of the thermal elements might be trusted whether the plates were thick or thin. A re-determination of the conductivities of N and O with the different arrangements of the prisms gave 0.000215 and 0.000199 respectively. When a disk of the standard rubber was turned down thin and its specific conductivity re-determined, it was found to be almost the same as before; but when disks F and I were made slightly thinner by turning off the polished surface on each side, the conductivity of the thinner disks was increased by 5 per cent.

and 3 per cent. This seems to show that in the cases of some sheets of hard rubber, the thermal conductivity of the skin near the polished surfaces is somewhat less than that of the mass of the material in the sheet. This difference, however, is too slight to account for the differences of conductivity shown by the table. It is well to emphasize the fact that the specific heat between 25° C. and 100° C. of the standard rubber is less (0·339) than that of such thin sheet rubber as I have experimented upon.

Stefan found for the thermal conductivity of a certain sheet of rubber, 0·787 centim. thick, the value 0·00026: this rubber had a somewhat greater density (1·22) and a much lower specific heat (0·23) than any of my specimens, so that the ratio of the conductivity to the specific heat per unit volume was somewhat greater. Experimenting upon a small disk of "ebonite" 1·93 centim. in diameter and 0·0414 centim. thick, Lees found the conductivity to be 0·00040.

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### III. *On Earthquake-Sounds.*

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**I**N a short paper published seven years ago †, I attempted to describe the phenomena of earthquake-sounds and to offer a theory of their origin. More detailed studies of recent British earthquakes, and especially of the Hereford earthquake of 1896, have added to our knowledge of the phenomena and slightly modified the theory. The catalogues of foreign seismologists have also furnished materials for investigation. I propose therefore to reconsider the subject in the present paper, dwelling chiefly on those points which have not yet received much attention.

#### *General Character of the Sound.*

The earthquake-sound is frequently described simply as a rumbling sound or, more fully, as a hollow or muffled rumbling sound, a harsh grumbling sound, a mysterious suppressed roar, or a strange deep sort of groan or moan. Occasionally, sounds of a totally different kind are observed, either alone or in conjunction with the preceding, sounds that are described by the terms rustling, whizzing, or hissing. The sound is generally of a more or less jarring nature, hardly ever becoming a musical tone, although it may approach to

\* Communicated by the Author.

† "On the Nature and Origin of Earthquake-Sounds": Geol. Mag. vol. ix. 1892, pp. 208-218.

such a character, as is evident from the comparisons to the deep notes of an organ, &c. The references to distant thunder and the moaning of the wind also testify to a certain smoothness or monotony in the sound. To some observers, however, the sound appears to be intermittent, to be like three loud explosive moans, or successive discharges of cannon, or a heavy body falling several times, say, down a short flight of stairs.

At places near the epicentre, the loudness of the sound is one of the chief features of a moderately strong earthquake. The sound is compared to the rumbling of six traction-engines, to that of a train going over a bridge, only intensified a hundred times, to a tremendous roaring, a sudden loud deafening noise, or a terrific explosion, louder than is produced by the heaviest artillery. Even in so slight an earthquake as that felt in the south of Cornwall on April 1, 1898, one observer described the sound as like the rumbling of thirty or forty waggons travelling at a rapid pace, while another remarked "that was the loudest thunder I ever heard." This may almost appear to be the language of exaggeration; but, from a careful study of the evidence, I think that it expresses the experience of certain, but not of all, observers. It will be seen afterwards how widely persons differ in their powers of hearing earthquake-sounds.

Another prominent characteristic of the sound is its extraordinary depth. The rolling of heavy railway-trucks, very low, is the evidence of one observer; of another, a low rumbling sound, much lower than the lowest thunder; while a third refers to the vibrations of the pedal notes of a great organ, only of a deeper pitch than can be taken in by the human ear. The idea of great depth is also given by the very frequent use of the word "heavy"\*. It is applied in every type of comparison, sometimes in an unusual manner, as, for example, in heavy thunder, a heavy conflagration, or a heavy explosion.

The earthquake-sound is frequently compared to the passing of heavy waggons and other vehicles. The comparison seems to be generally suggested when the sound is of long duration, of a certain smoothness, and gradually increases in intensity to a maximum and then dies away †. The reference is often

\* In strong earthquakes, the percentage of descriptions in which the word "heavy" occurs, varies from 28 in the Hereford earthquake of 1896 to 45 in the Pembroke earthquake of 1893. In very slight earthquakes it may fall as low as 13.

† In the Leicester earthquake of 1893, 27 observers stated that the sound gradually increased in intensity and then died away; and of these 20 compared the sound to that of passing vehicles.

to a vehicle driven *quickly* past, to illustrate apparently the evenness of the sound or the rapidity with which it attains and recedes from its maximum intensity. The common illusion that an underground train rushes up to and beneath a house, and continues its journey in the opposite direction, is no doubt due to this gradual rise and fall in intensity.

### *Types of Earthquake-Sound.*

A few observers find it difficult to describe the sound, but most compare it to some well-known type, and the resemblance in many cases is so close that the observer at first attributed it to the object of comparison. The descriptions which I have examined, several thousands in number, may be classified under the following heads :—

(1) *Waggons &c. passing.*—One or several traction-engines, either alone or heavily laden, sometimes driven furiously past ; a steam-roller travelling at a quicker pace than usual or passing over frozen ground ; heavy waggons coming quickly down a hill, driven over stone paving, on a hard or frosty road, in a covered way or narrow street, or over hollow ground or a bridge ; a heavy roller on a garden path, or a wheelbarrow on a hard and frosty road ; express or heavy goods trains rushing through a tunnel or a deep cutting, crossing a wooden bridge or iron viaduct, or a heavy train running on snow ; also, the dragging of heavy furniture or boxes across an adjoining floor, the grating of a boat on a beach or of the bottom of a large vessel when dragged over rocks.

(2) *Thunder.*—A loud clap or heavy peal, sometimes dull, hollow, muffled, or subdued, but most often distant, and thus conveying the impression of a low deep booming sound.

(3) *Wind.*—A moaning, roaring, howling, rushing, hissing, or rough, strong wind ; the rising of the wind, the roaring of a great squall, a heavy wind pressing against the house, or a high wind sweeping through trees ; the howling of wind in a chimney, a chimney on fire, and the blare of a furnace when the door is opened.

(4) *Loads of stones &c. falling.*—The tipping of a load of coal, stones, or bricks ; a wall or roof falling, or the crash of a chimney through the roof.

(5) *Fall of heavy bodies.*—The fall of a heavy weight, of a tree or heavy timber ; the thud of a large mass of snow from a house-top, the banging of a door, only more muffled, and the blow of a wave on the sea-shore.

(6) *Explosions.*—The explosion of a boiler, a cartridge of

lynamite, or a rocket ; a distant colliery explosion ; distant heavy rock-blasting, and the boom of a distant cannon.

(7) *Miscellaneous.*—The trampling of many animals, such as cows rushing on the turf below, a quick stampede of a large herd of elephants, a number of powerful men struggling desperately in the room overhead ; an immense covey of partridges or a flock of starlings on the wing ; the roar of a waterfall, the heavy rumbling of sea-waves in a cave, and the breaking of waves on a pebbly beach ; the passage of a party of skaters, the falling of fine rain or hail on the leaves of trees, a low pedal note on the organ ; and the rending or settling together of huge masses of rock.

*Frequency of Comparison to different Types.*—The type of comparison employed varies not only in different earthquakes, but in different parts of the disturbed area of one and the same earthquake. This is shown by Table I., in which the figures denote the percentage of entries under each type with regard to the total number of comparisons.

TABLE I.

Earthquake.	Intensity.	Waggons &c. passing.	Thunder.	Wind.	Load of stones falling.	Fall of heavy body.	Explosions.	Miscellaneous.
Cornwall, May 17, 1892 ...	4	22·7	22·7	...	6·8	2·3	43·1	2·3
" Aug. 27, 1895 ...	4	33·4	46·7	...	...	...	20·0	...
" Jan. 26, 1896 ...	3 or 4	26·7	56·7	...	...	...	16·7	...
" Apr. 1, 1898 ...	4	25·0	36·4	5·7	2·3	2·3	23·9	4·5
Hereford, Oct. 6, 1863 ...	8	37·4	25·7	7·6	2·9	6·4	12·8	7·0
Essex, Apr. 22, 1884 .....	8	40·0	32·0	16·0	4·0	...	8·0	...
Inverness, Nov. 15, 1890 ...	7	62·3	10·0	7·8	3·3	5·6	8·9	2·2
Pembroke, Aug. 18, 1892 ...	7	44·5	29·0	6·7	2·2	1·8	4·9	11·1
Leicester, Aug. 4, 1893 ...	5	51·1	33·7	...	2·2	1·6	9·2	2·2
Pembroke, Nov. 2, 1893 ...	7	51·0	20·4	6·0	3·2	3·2	8·8	7·4
Exmoor, Jan. 23, 1894 ...	4	40·5	43·2	5·4	...	2·7	5·4	2·7
Hereford, Dec. 17, 1896 ...	8	45·4	15·0	15·5	3·9	2·7	7·2	10·3

The four Cornish earthquakes were all weak and originated in foci of comparatively small linear dimensions. The Exmoor earthquake, though not much stronger, resembled the remaining shocks in having a long focus. In these cases, reference is made more frequently than in the first to passing waggons &c. and less frequently to explosions and the firing of heavy guns. Again, in the Comrie earthquakes of 1839, the sound which accompanied the more violent shocks appeared "to resemble thunder more than

anything else,—certainly much deeper toned and more awful,” while that which was heard with the weaker and shorter shocks was compared to “the noise caused by the blasting of a soft rock at a considerable distance, followed by the reverberation of the surrounding mountains.” The type of comparison employed therefore depends on the duration of the sound, and this again on the length of the seismic focus.

### *Variation in the Nature of the Sound.*

*Variation in Intensity.*—Even if there were no definite reports on this point, it would be evident, from the frequent references to passing vehicles, that the sound is often of varying intensity. Sometimes the sound becomes gradually louder and ceases almost abruptly, or it may begin suddenly and die away gradually; but in these cases the more or less rapid termination is probably subjective and due to the observer’s inability to hear deep sounds. In each of the three most important British earthquakes of the last decade (namely, the Pembroke earthquakes of 1892 and 1893, and the Hereford earthquake of 1896), more than 90 per cent. of the observers who refer to the point distinguish some change in the intensity of the sound; while the percentages of those who heard the sound become gradually louder and then die away are respectively 68, 85, and 56.

The relation which the change in intensity of the sound bears to that of the shock is important. Generally, the two increase and decrease together, though, as will be seen afterwards, there are exceptions to this statement. Or, when the shock is slight, it is felt when the sound is loudest, as at Helston, during the Cornwall earthquake of May 17, 1892, when “a distant rumble was heard, gradually increasing in intensity until it became a violent thundering sound, at which instant everything in the room was perceptibly shaken, the sound dying away with the shock with the same sound as before”\*.

*Variation in Character.*—As a general rule, the sound adheres throughout to one of the types enumerated above, and varies, if at all, only in intensity. In the neighbourhood of the epicentre, however, there is also a change in character perceptible to some, but not all, observers, the change taking

\* Mr. David Milne (Edin. New Phil. Journ. vol. xxxi. 1841, p. 261) remarks that, in British earthquakes, there may be two perfectly distinct sensations, a tremulous motion, and a violent blow or concussion. “The tremulous or trembling motion,” he says, “is always perceived. When the blow occurs, it is generally in the midst of the tremors, and accompanied with the loudest noise.”

place at the time when the shock is strongest. It then assumes a rougher, more grinding or grating character, occasionally, but not often, being heard as a loud report or crash. As this is a feature which does not seem to have attracted much attention, the following examples from different British earthquakes are given in illustration.

At Penryn, the Cornwall earthquake of 1892 consisted of two distinct vibrations, each followed by tremulous motion ; each was also accompanied by a sound like the crash of a heavy weight on the floor above and followed by a rumbling sound like that of a waggon roaring along the street, continuing after the shock and dying away in the distance. At Lamphey, during the Pembroke earthquake of 1892, a sound was heard for three seconds resembling that of sea-waves at a distance, followed for two seconds by a deep heavy boom of thunder, during which the shock was felt, and this by a sound like sea-waves dying away in about three seconds.

Many observations of this kind were made during the Hereford earthquake of 1896. For instance, at Dilwyn in Herefordshire, there was a rumbling as of a train going over a bridge, with a terrific crash, such as is heard in a thunderstorm, at the instant when the shock was strongest, the rumbling dying away afterwards for some seconds. Again, at Horsley in Gloucestershire, the sound was first like a violent wind among trees ; then, while the shock lasted, like a very heavy traction-engine close to the house, and, at the instant when the sound was loudest and the shock strongest, the rumbling was accompanied by a sort of grinding noise, which appeared to be under the observer's house, and sounded as if a landslip was in progress.

When the sound is compared to wind, a change is frequently observed. Thus, Prof. Papavasiliou records, on the authority of M. de Biasi, that a strong shock felt in Zante on June 31 (*sic*), 1896, ‘ fut précédée d'un bruit pareil d'abord à celui du vent, puis à celui d'une voiture ’ ; and a similar change was observed in the same island on Sept. 23, 1896\*. During the Hereford earthquake of 1896, the change generally took place at or about the instant when the shock began or ceased to be felt ; as at Batley, in Yorkshire, where the shock was preceded by a sound as of a rushing wind, and was accompanied by a low rumbling noise like distant thunder.

Though some exceptions to the conclusion will be noticed later, it thus appears that, as an earthquake-shock increases

\* Observatoire National d'Athènes, *Bull. Mens. Séismol.* 1 année, 1896.

and decreases in intensity, the sound grows louder and dies away, and also deepens and rises in pitch ; in other words, the vibrations which are observed as shock and sound increase and decrease together in amplitude and period.

*Variation in the Nature of the Sound throughout  
the Disturbed Area.*

In one respect the sound exhibits a marked uniformity all over the sound-area, namely, in its great depth, if we may judge from the frequency with which the word "heavy" occurs in the descriptions. In the Hereford earthquake, the word is used in 27 per cent. of the comparisons from the seven central counties, in 30 per cent. from the counties surrounding these, and in 27 per cent. from those which lie outside. In the Pembroke earthquake of 1892, the corresponding percentages are 38, 45, and 31, and in that of 1893 they are 51, 37, and 39 \*.

*Variation in Type.*—The connexion between frequency of type-reference and distance from the epicentre is shown roughly in the Table (p. 38).

The principal change common to all three earthquakes is thus the increasing percentage with the distance of the comparisons to wind ; and we may infer from this that the sound tends to become smoother and more nearly monotonous as we recede from the epicentre. As a rule, the comparisons to passing waggons &c. are less numerous at a distance than near the epicentre. The reasons for this appear to be that the duration of the sound diminishes as the distance increases, and that the rise and fall in intensity are also less marked. In the Hereford earthquake it is possible to draw curves of equal percentage of reference to this type, and these show that the frequency of reference depends on the duration of the sound.

*Variation in Change of Intensity.*—One effect of distance would naturally be to quench the weaker sound-vibrations at the beginning and end, and we should expect to find less variation in the intensity of the sound at a distance than near

\* In the Hereford earthquake, the central counties are those of Hereford, Gloucester, Worcester, Shropshire, Radnor, Brecon, and Monmouth ; the inner ring consists of Somerset, Wiltshire, Berkshire, Oxford, Warwick, Birmingham, Stafford, Cheshire, Flint, Denbigh, Montgomery, and Glamorgan ; and the outer ring of the remaining counties in which the sound was heard. In the Pembroke earthquakes the central counties are Pembroke, Carmarthen, and Cardigan ; those in the inner ring are Cornwall, Devon, Glamorgan, Brecon, Radnor, Montgomery, and Merioneth ; while the outer ring consists of the remaining counties of the sound-area.

TABLE II.

Earthquake and District.	Waggons &c. passing.	Thunder.	Wind.	Load of stones falling.	Fall of heavy body.	Explosions.	Miscel- laneous.
{ Central counties.....	40.7	29.7	3.3	3.3	1.1	6.6	15.4
Inner ring .....	54.3	30.0	5.7	2.9	1.4	1.4	4.3
Outer ring .....	41.4	27.6	13.8	...	1.7	1.7	13.8
Ditto. (English counties) .....	22.7	45.5	13.6	...	4.5	...	13.6
{ Central counties.....	65.7	14.0	3.2	2.1	2.1	7.5	5.4
Inner ring .....	43.6	23.1	7.7	2.6	5.1	12.8	5.1
Outer ring .....	37.3	25.3	10.9	4.8	7.2	6.0	8.4
Ditto. (English counties) .....	33.8	26.0	11.7	5.2	7.8	6.5	9.0
{ Central counties.....	44.9	17.5	13.7	4.4	2.0	8.2	9.3
Inner ring .....	42.6	13.9	16.0	4.5	3.9	6.9	12.1
Outer ring .....	49.0	11.5	18.3	2.2	2.8	5.6	10.6

the epicentre. This certainly is the case, but the change is not a marked one ; for, in the Hereford earthquake, of all the observers who refer to the point, the percentages of those who heard the sound increase to a maximum and then die away are 57.3 for the central counties, 53.7 for the inner ring, and 53.1 for the outer ring. The corresponding percentages for those who considered the sound of uniform intensity throughout are 8.0, 11.1, and 12.2.

The test employed, however, is not a very clear one, for at all stations but those near the boundary of the sound-area some change in the intensity would be perceptible. A better test is furnished by the observed nature of the sound, by the increasing frequency of reference to the wind-type as we recede from the epicentre, and by the comparison of the sound at great distances to distant thunder.

*Variation in Change of Character.*—In the Hereford earthquake, the percentage of the total number of accounts in which any change was recorded is 19.4 in the central counties, 10.7 in the inner ring, and 2.8 in the outer ring, of counties. In the first district the change of type is generally due to the perception of the crashing or grinding sound which accompanied the strongest vibrations ; in the others, the change, when observed, is almost invariably from a sound like wind to a more rumbling sound at the time of the shock, or *vice versa*. In every earthquake I have studied, it is only near the epicentre that the explosive reports or crashes in the midst of the rumbling sound are heard. At a moderate distance, the sound before and after the shock becomes smoother, while the sound which accompanies the shock retains to a certain extent its rougher and more rumbling character. As we approach the boundary of the disturbed area, the irregularities are still further smoothed away, and the only sound heard is like the low, almost monotonous roll of distant thunder.

*Variability in the Sound due to its Neighbourhood to the  
Lower Limit of Audibility.*

*Inaudibility to some Observers.*—Attention has been drawn in the preceding pages to the extraordinary depth of the earthquake-sound, so far as it can be inferred from the efforts that are made to describe it. But the most decisive evidence of the close neighbourhood of the sound to the lower limit of audibility is furnished by the fact that the same vibrations are heard by some and not by others. One observer will describe the sound as like the rumbling pro-

duced by a heavy traction-engine passing, while another will be equally positive that the shock was unaccompanied by sound. Not only people in the same town, but persons in the same house, and even in the same room, differ in this respect. There is no reason, it should be remarked, for supposing that they were not equally alert, or that their conditions varied essentially except in their powers of perceiving deep sound.

This point is so important that I venture to give further evidence in illustration.

M. Ch. Deville, who studied the Guadeloupe earthquake of Feb. 8, 1843, remarks that "ce bruit . . . n'est pas perçu par tout le monde. Ni moi, ni les personnes qui m'entouraient, ne l'avons entendu à la Dominique ; bien plus, peut-être par suite de l'émotion, une foule de témoins du désastre de la Pointe-à-Pitre disent ne l'avoir point entendu. Quelques uns affirment, au contraire, que ce bruit s'est prolongé un petit nombre de secondes encore après la commotion ; pour d'autres, il a été sensible dans quelques unes des secousses de moindre violence qui se sont succédé depuis celle du 8. On prétend même que chacune de ces dernières est annoncée par un bruit souterrain dans les îlets de la rade de la Pointe-à-Pitre" \*.

"In the Tokio seismic area," says Prof. Milne, "sounds accompanying earthquakes are rare. Although the author has observed many earthquakes when sounds are said to have been heard, it has only been once during a period of several years that he can say that he distinctly heard a sound. This was on March 11th, 1881, when a sound between hissing and rumbling was heard" †.

During the Hereford earthquake of 1896, if we take the evidence only of those observers who were awake before it began, we find that two out of five observers at Clifton did not hear the sound, at Leamington two out of six, in Birmingham and the neighbourhood four out of 23, in London eight out of 18, and at Bangor two out of seven. In the whole disturbed area, 148 persons who were awake heard no sound, and all but five of these were within the boundary of the sound-area.

*Partial Inaudibility to some Observers.*—Similar evidence is afforded by the partial inaudibility of the sound, by its total cessation, generally during the shock itself, to some observers, while others continue to hear it. In Great Britain

\* Observations sur le tremblement de terre éprouvé à la Guadeloupe le 8 février 1843 (Basse-Terre, 1843), p. 4.

† Japan Seismol. Soc. Trans. vol. xii. 1888, p. 56.

records of this kind occur in many earthquakes. For instance, during the Hereford earthquake  $8\frac{1}{2}$  per cent. of the observers who were certainly awake, and heard the sound, state expressly that they were unconscious of any sound while the shock lasted. Generally it was heard only before the shock, ceasing either gradually or somewhat abruptly about the time when the shock began ; but it was sometimes heard only when the shock was dying away, and in two cases before and after, but not during, the shock. That this cessation of the sound was inherent in the observers and not due to their position, is evident from the experiences of others in the same places. At Presteign, in Radnorshire, to one observer the sound ceased before the vibrations commenced ; to another the sound was terrible, as of rending rocks beneath his feet, and was loudest at the time when the shock was strongest. At Birmingham one observer heard the sound before, during, and after the shock, another entirely before it, a third only after it, while others, as already remarked, heard no sound at all.

*Variability in the Nature of the Sound.*—Even when observers in the same place agree in hearing the sound, it may present itself to them under different forms. In the Hereford earthquake we find that at Hereford a crash or bomb-like explosion was noticed during the rumbling sound by four observers, while four others describe the sound in terms which imply uniformity of character. At Pridewood (four miles from the epicentre) one observer, who felt two series of vibrations and heard a loud crash with the maximum of each, remarks that only a few heard this peculiar sound, although most persons noticed a premonitory rumbling. At Ledbury the sound, according to one, began like a rushing wind, and culminated in a loud explosive report ; another heard a noise like distant thunder, which ended when the shock began ; while a third heard no sound at all. The same diversity, both in character and intensity, is noticeable at places further away from the epicentre. At Clifton one person heard a slight rumbling noise, while another compared the sound with that of a heavy traction-engine passing. In the Birmingham district the accounts refer on the one hand to the distant approach of a train and the rising of the wind, on the other to the reports of large cannons and to a noise as if tons of debris had been hurled against the wall of a house.

*Explanation of the above Phenomena.*—These observations show clearly that there is a lower limit of audibility, and, further, that this limit is not the same for all persons. Now, to create an equally strong impression on the ear, the

strength of the vibrations must be very much greater for deep sounds than for high ones, and this is especially the case for the deepest sounds of all. If, then, the sound is *just* audible to any person, it will cease to be heard if the period of the vibrations be increased without any change occurring in their strength, or if the strength be diminished, while the period remains unchanged.

In the immediate neighbourhood of the epicentre, the sound-vibrations are of such intensity that they are heard by nearly all observers, at any rate in Great Britain. As we recede from the epicentre the vibrations diminish in strength, and at the same time, as we know from seismographic records, the larger vibrations increase in period. On both accounts, then, they tend to become inaudible. Thus the percentage of persons who hear the sound should diminish as the distance from the epicentre increases, until we reach the boundary of the sound-area where no human being is capable of hearing so deep a sound.

If the vibrations which reach a particular observer are at first very rapid, and then gradually increase in period without an appropriate concomitant increase in strength, the sound will become gradually deeper, and finally will cease to be heard, the ending being more or less abrupt. Again, if the period were to be subject to a succession of changes without the proper change of strength, it is possible that to some observers the vibrations might be inaudible during short intervals when the period is great, and they would then hear the sound as a succession of reports, a series of footfalls, &c.

Further, the vibrations which reach the observers in one place at any moment are probably of various amplitude and period. One may hear many vibrations, and another only some of the series. Thus to one observer the sound may be like a rising wind, to another like a heavy traction-engine passing ; one may hear the crashes which accompany the principal vibrations, while a second will be deaf to them ; to one the sound may become continually louder and cease abruptly, to another it may increase to a maximum and then gradually die away.

As we recede from the epicentre, however, the vibrations of every period tend to become inaudible. The limiting vibrations of the whole series will be the first to be lost, especially those of longest period. Thus near the epicentre sound-vibrations of many different periods will be heard, and the sound will be more complex than it is elsewhere. It is only in this region that the loud crashes will be heard with the strongest vibrations. As the observer recedes from the

epicentre these changes in character must become gradually less marked, until at a great distance, near the boundary of the sound-area, the audible vibrations lie within very narrow limits with regard to period, and the sound becomes an almost monotonous deep growl of nearly uniform intensity.

### *Isacoustic Lines.*

An *isacoustic line* may be defined as a line which passes through all places in which the percentage of persons who hear the sound is the same.

The construction of isacoustic lines depends on the following principles :—(1) at most places within the sound-area the sound lies between the extreme values of the lower limit of audibility, so that it is heard by some and not by others ; (2) as the distance from the centre increases the audibility of the sound-vibrations diminishes, so that the sound is heard by a decreasing proportion of observers ; (3) the people in any district possess various powers of hearing low sounds, but in any one country the percentage of its inhabitants who are capable of hearing a given low sound is probably in all parts very nearly the same.

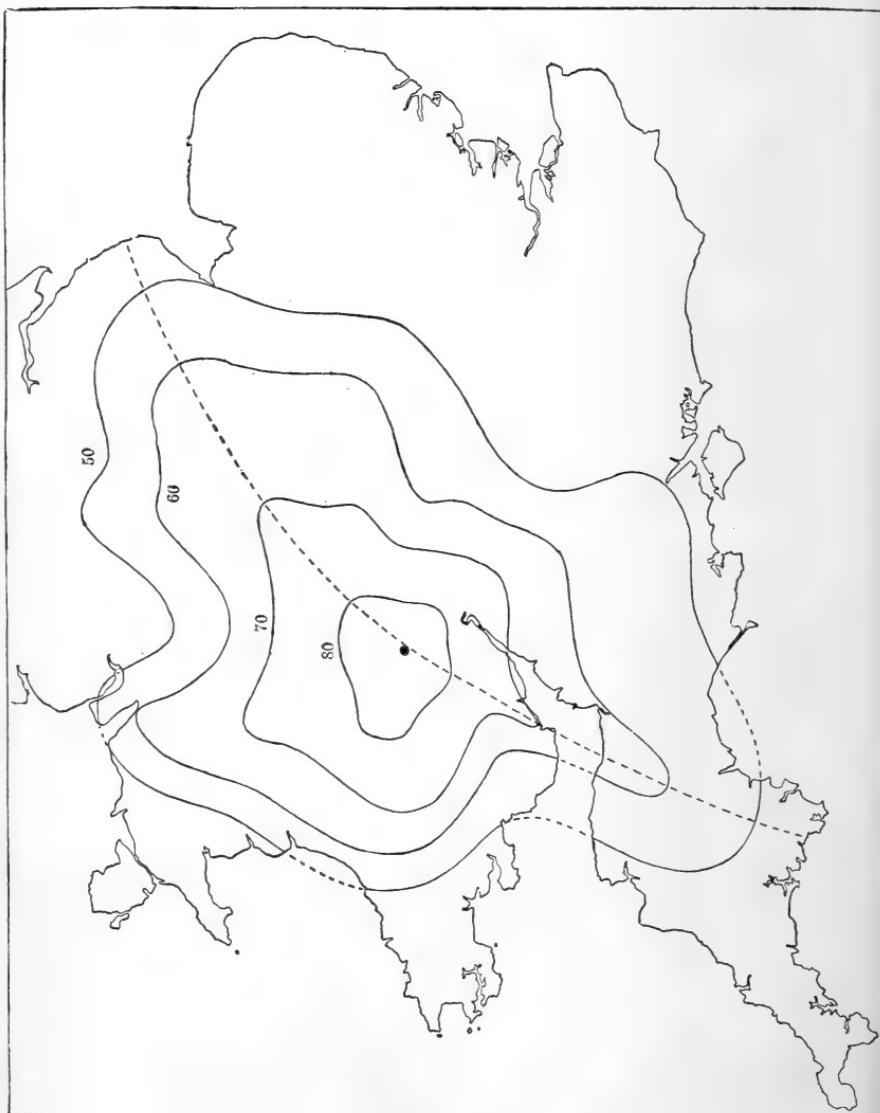
In fig. 1 (p. 44) the continuous lines represent the isacoustic lines of the Hereford earthquake of 1896. Their construction depends on the percentage of observers within each county who recorded their perception of the sound. The percentage varies from 87·2 in Herefordshire to 23·1 in Essex, and for any county it is supposed to correspond to that of a small district immediately surrounding its centre, and for adjoining counties to vary uniformly from one centre to another. The counties are of course too large and also too unequal in area to allow of great accuracy in the construction of the lines, and the number of observations in some of the counties at a distance from the epicentre is not so great as is to be desired\*.

\* The inner isoseismal lines of this earthquake are elongated ovals with their longer axes nearly north-west and south-east ; and the peculiar form of the isacoustic lines is due to the fact that there were two distinct foci arranged along a north-west and south-east line, the north-west focus (near Hereford) being first in action by a few seconds. The series of vibrations from the two foci coalesced and formed one series at places within a hyperbolic band, the curvilinear axis of which coincides very nearly with the dotted line (fig. 1) passing through the points of greatest extension of the isacoustic lines. The disturbance was much stronger at the north-west than at the south-east focus, while the inequality between the sound-vibrations from the two foci was inconsiderable. There was therefore no marked distortion of the isoseismal lines in the neighbourhood of the hyperbolic band, while the isacoustic lines are completely diverted from their normal course.

*Audibility of Earthquake-Sounds in different Countries.*

While it appears to be the rule in some countries that earthquakes shall be accompanied by sound, in others it

Fig. 1.



would seem to be rather the exception. The exact percentage of earthquakes attended by sound is, however, difficult to determine, on account of the slight attention paid

to sound-phenomena by many compilers of earthquake-catalogues; so that it often remains uncertain whether we are to attribute the lack of reference to the inaudibility of the vibrations or to the neglect of the compiler or his authorities. For instance, in Barbiani's list of earthquakes in Zante (1825–1863) \* only 21 out of 1371 shocks are recorded as accompanied by sound. According to Mr. Roper's catalogue †, only 21 per cent. of the British earthquakes felt during the present century (1801–1889) were attended by sound; but we know from other records that this low figure is chiefly due to incomplete chronicling.

*Great Britain*.—Mr. David Milne, in a valuable memoir on "Earthquake-Shocks felt in Great Britain, &c.," remarks that "the shocks are invariably accompanied by sounds" ‡. Though his list contains many entries in which no mention of sound-phenomena is made, I believe that this statement is practically correct. Among the undoubted earthquakes of the last ten years I know of only one exception. The well-known Comrie earthquakes are hardly, if ever, free from sound; indeed, the observers speak of "hearing the earthquakes," rather than of feeling them.

TABLE III.

Earthquake.	Percentage of Audibility in	
	Disturbed Area.	Central District.
Inverness, 1890 .....	93·8	...
Cornwall, 1892.....	95·3	...
Pembroke, 1892, Aug. 18, 0.24 A.M. ....	75·4	97·2
"      "      1.40 A.M. ....	90·8	...
"      "      2.50 A.M. ....	43·9	...
Leicester, 1893.....	90·7	...
Pembroke, 1893 .....	58·7	98·8
Exmoor, 1894 .....	100·0	...
Cornwall, 1895.....	100·0	...
"      1896....	100·0	...
Hereford, 1896.....	59·2	87·2
Cornwall, 1898.....	93·8	..

\* *Dijon, Mém. Acad.* vol. xi. 1863, pp. 1–112.

† "A List of the more remarkable Earthquakes in Great Britain and Ireland during the Christian Era." By W. Roper (Lancaster, 1889).

‡ *Edinburgh New Phil. Journ.* vol. xxxi. 1841, p. 287.

The proportion of observers who hear the sound is generally very great in British earthquakes, as will be seen from Table III. With one exception the percentage is higher for slight than for strong shocks. This of course is partly due to the sound-area in the latter cases being somewhat less than the disturbed area, but not to any great extent, for the number of observers outside the sound-area is always small. It is rather due, I think, to the sound being by far the most prominent feature in a weak earthquake.

*Italy.*—The organization for the study of earthquakes is more complete in this country than in any other except Japan. The results are published by the Central Office of Meteorology and Geodynamics at Rome\*. Owing to the uncertainty in some of the time-records, it is not always possible to group together the observations of the same earthquake, and a small error may thus enter into the estimates. In the two years 1895–1896 the total number of earthquakes (excluding those of distant origin, and others registered only by instruments) is 692, and of these 217, or 31·4 per cent., are recorded as accompanied by sound. In different earthquakes the percentage of records in which sound-phenomena are mentioned is very variable, ranging from 18 for the earthquake of June 10, 1895, to 47 for that of April 13, 1895. In the Verona earthquake of June 7, 1891, 34 per cent. of the observers heard the sound. Out of 274 after-shocks of this earthquake, only 25, or 9 per cent., were attended by sound; and of one of the strongest of these shocks, that of Aug. 31, only five out of 101 observers were recorded as auditors of the sound †.

Admirable as are the observations collected by the Central Office, it is important, from the present point of view, to notice how large a number (more than 60 per cent.) consist of records from single places, though there were often several observers at each place mentioned. The next Table shows the relation between the number of records of each earthquake and the audibility of the accompanying sound-phenomena.

This Table shows very clearly how the audibility of the sound increases with the number of records of the earthquake. It might of course be argued from this that the number of records depends on the extent of the disturbed area, and this again on the strength of the shock; in other words, that the sound is more frequently audible with strong, than with

\* In supplements to the *Boll. della Soc. Sismol. Ital.*

† M. Baratta, *Annali dell' Uff. Centr. Meteor. e Geod.* vol. xi. parte 3 (1892).

TABLE IV.

	Number of Records.							
	1	2	3	4	5	6	7-10	>10
Number of earthquakes .....	595	91	54	26	13	17	32	45
Number of earthquakes accompanied by sound.....	124	36	24	15	8	11	26	43
Percentage of earthquakes accompanied by sound.....	20·8	39·6	44·4	57·7	61·5	64·7	81·2	95·5

weak earthquakes. But in Great Britain, at any rate, this is not the case ; for the weaker shocks would often pass entirely unnoticed if it were not for the far greater prominence of the sound. The more probable interpretation is that, with the larger number of records, there is the greater chance of finding among the observers one or more who are capable of hearing very deep sounds. Though the average observer in Italy may be inferior in this respect to the average observer in Great Britain, it is difficult, I think, to resist the conclusion that, with a large enough number of records, every Italian earthquake would be found to be accompanied by sound.

*Japan*.—For this country we have Prof. Milne's valuable catalogue of 8331 earthquakes recorded between 1885 and 1892\*. Many of the shocks originated beneath the sea, and in the following estimates these have been omitted, for, in some cases, it is possible that the sound-area may not have reached the land. There remain 5902 earthquakes, of which 1562, or 26·5 per cent., were accompanied by sound.

The percentage varies from year to year, being for the eight years included in the record, 38·0, 42·0, 30·4, 30·0, 33·7, 20·4, 20·6, and 29·2 respectively. The low percentages for the years 1890 and 1891 are due to the preponderance of earthquakes in certain districts where the sounds are somewhat rarely heard.

In his great catalogue from which the above results are obtained, Prof. Milne gives approximately the disturbed area and the position of the epicentre of nearly every earthquake. For the latter purpose the whole country is divided into rectangles, the sides of which are a sixth of a degree of latitude and longitude in length. Prof. Milne has studied the distribution of earthquakes accompanied by sound by placing a mark in the epicentral rectangle of each such earthquake. He has shown that the number of these earthquakes

\* Japan Seismol. Journ. vol. iv., 1895.

varies considerably in different districts, and has endeavoured to trace the connexion between the frequency of sound-accompanied earthquakes and the geological structure of the district. I shall refer to these conclusions in the next section.

It is clear, however, that the number of earthquakes accompanied by sound must be a function of the total number of earthquakes, and, therefore, that a better method would be to study the variation in the ratio of the former number to the latter. I have tried to do this for the whole of Japan, but, great as is the number of recorded shocks, it is not sufficient for the purpose ; though a map of a smaller district, in which earthquakes were exceedingly numerous, is given in fig. 2. Taking only those rectangles which contain not less than 20 epicentres during the years 1885–1892, the percentage of the total number of earthquakes that were accompanied by sound may be as high as 77, and as low as zero. In two rectangles, chiefly affected by the after-shocks of the Kumamoto earthquake of 1889, the percentage is only 7.

A point of great importance is the relation between the audibility of an earthquake and its disturbed area. This is shown in Table V.

TABLE V.

	Disturbed Area in square miles.						
	<100	100–500	500–1000	1000–2000	2000–5000	5000–10,000	>10,000
Number of earthquakes	1848	2169	672	403	308	195	218
Number of earthquakes accompanied by sound	223	556	163	160	158	132	153
Percentage of earthquakes accompanied by sound	12.1	25.6	24.3	39.7	51.3	67.7	70.2

If we omit the years 1890–1892, on account of the large numbers of aftershocks of the Kumamoto and Mino-Owari earthquakes that were unaccompanied by sound, the corresponding percentages are

25.9, 24.4, 41.7, 45.5, 62.9, 69.8, and 59.7.

Thus we see that, with some comparatively unimportant exceptions, the audibility of an earthquake increases with its disturbed area, that is, roughly, with its intensity. But the

most important fact brought out by this analysis is that the highest percentage is only 70. The continual approach towards a percentage of 100, which is characteristic of Italian earthquakes, is here absent. That in eight years as many as 65 earthquakes should disturb areas of more than 10,000 square miles and yet be unaccompanied by recorded sound, while the audibility increases as a rule with the disturbed area, is indicative, in all probability, of the defective powers for hearing deep sounds possessed by the Japanese people\*.

*Other Countries.*—The evidence for other countries is much less complete than in the preceding, and I will therefore merely give a few examples. Of 521 Greek earthquakes in 1896 recorded by Dr. S. A. Papavasiliou, 160, or 30·7 per cent., were accompanied by sound. Of these, 309 were felt in the island of Zante, and 101, or 32·7 per cent., of these were attended by sound†. Of 39 earthquakes recorded in New Zealand in 1891, sound was heard with 18, or 46 per cent.‡. In the Charleston earthquake of 1886 the audibility-percentage is low in nearly every State, being 19·5 in the central State of South Carolina, and, among the neighbouring States, 21·2 in Virginia, 30·8 in North Carolina, 17·9 in Tennessee, 20·5 in Georgia, 12·5 in Alabama, and 23·0 per cent. in Florida; but it is possible that these low figures are due to the incompleteness of the records§. The most reliable records for any non-British earthquake are probably those which are obtained from Prof. F. Suess's study of the Laibach earthquake of April 14, 1895. In this case the audibility-percentage is 60·8 for the whole disturbed area, and 96·7 for the central province of Carinthia||.

#### *Relation between Sound-Audibility and Geological Structure.*

In earthquakes which are strong enough to be recorded by seismographs, both the period and amplitude of the vibrations depend on the nature of the surface-rocks. It is therefore reasonable to suppose that some relation must exist between the audibility of the short-period vibrations and the nature

\* The type of comparison is only mentioned in 13 cases in Prof. Milne's catalogue, but it is worthy of notice that 10 comparisons are made to wind, 1 to thunder, and 2 to explosions.

† "Observatoire National d'Athènes," *Bull. Mens. Séismol.* 1 année, 1896.

‡ G. Hogben, *Austral. Assoc. Rep.* 1892, pp. 1-33.

§ C. E. Dutton, *Amer. Geol. Surv.*, Ninth Rep. pp. 410-528.

|| *Wien. Geol. Jahrb.* 1896, p. 523.

of the rocks in which the earthquake originates or of those on which the observers are situated. Mr. C. A. Stevenson remarks that in the Scottish earthquake of November 28, 1880, most of the observers near the epicentre who heard the sound were stationed on hard dense rocks with little or no soil near them\*. But the records of this earthquake are too few to establish a general law.

Prof. Milne's discussion of the sound-phenomena of the Japanese earthquakes is founded on a very large number of records. In the whole country he indicates fifteen districts in which earthquakes are specially numerous, and examines the sound-phenomena with respect to its geological structure. The conclusion at which he arrives is that "generally sound is heard in rocky mountainous districts, while in the alluvial plains it is but rarely observed"†.

The relative, rather than the absolute, frequency of sound-accompanied earthquakes being, however, the more correct test, I have calculated the percentage of the earthquakes in each district that were attended by sound and that originated under land. They are as follows:—21·6, 18·6, 1·8, 18·7, 30·0, 29·9, 23·1, 34·5, 26·7, 33·3, 8·0, 50·9, 42·2, 16·9, and 50·0. Prof. Milne's general conclusion is in part supported, and in part contradicted, by this more definite evidence. On the one hand, we have the comparatively high percentages of 42·2 and 34·5 in the mountainous districts 13 and 8 respectively. On the other, we have a percentage of 18·7 in district 4, where "the coast is rocky, built up of palæozoic strata"; while in the mountainous district 9 the percentage (26·7) is practically equal to the average for the whole country (26·5). The high percentage of 50 in district 15, which consists "of a sandy coast bordering a plain," is not very reliable, as it rests on no more than eight earthquakes.

Possibly the districts are too large for the deduction of general laws. But, if we take only the rectangles, whose areas vary from 114·3 square miles in the south of the country to 92·8 square miles in the north, we find great variety of audibility-percentage within the limits of a district. For instance, in four consecutive rectangles ‡, bounded by the same parallels, in the Mino-Owari plain, the percentages are 14·3, 41·0, 12·2, and 23·5. Immediately to the south of the first two of these rectangles are others § in which the percentages are 77·4 and 11·5.

If, however, the audibility of an earthquake depended only

\* Edinburgh Roy. Soc. Trans. vol. xi. 1881, pp. 184, 185.

† Japan Seismol. Journ. vol. iv. 1895, pp. xviii–xix.

‡ 1401–1404, district 7.

§ 1456 and 1457, district 7.

on the nature of the rock beneath which it originated, the percentage of audibility should not vary perceptibly at different times; and this is very far from being the case. Taking the district 7 as a whole, the percentage in November 1891 (immediately after the Mino-Owari earthquake) was 17·9, and during the next five months it lay between 10·5 and 12·1; then it suddenly rose to 38·8 in May 1892, and during the following seven months never fell below 32·4, while it maintained an average of 41·8. In the smaller rectangles we find the same variety; in one (that numbered 1457), for instance, the percentage was 7·7 during the three months November 1891–January 1892, and 39·0 during the next eleven months; in another (1402) the percentages during the same intervals were 10·3 and 55·4 respectively.

Thus whatever the nature of the relation between the audibility of Japanese earthquakes and the geological structure may be, it seems to be often masked by other conditions of greater importance, one of which will now be considered.

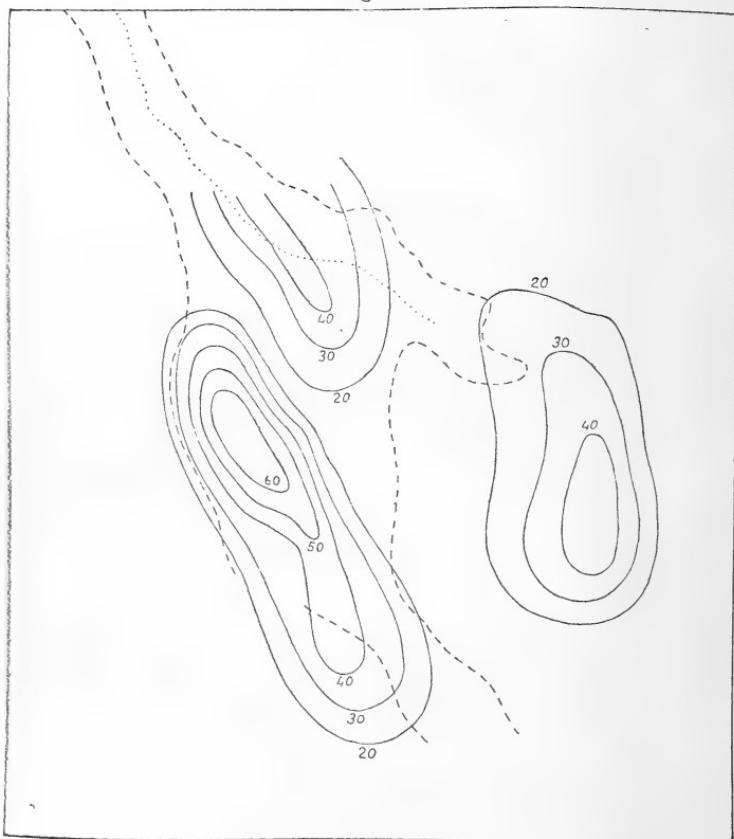
#### *Equal-Audibility Curves in the Mino-Owari District (Japan).*

The district represented in the accompanying map (fig. 2) is that part of Japan in which the Mino-Owari earthquake of 1891 and the majority of the very numerous after-shocks were most prominently felt. It is bounded by the parallels  $34^{\circ} 40'$  and  $35^{\circ} 50'$  of north latitude and by the meridians  $2^{\circ} 10'$  and  $3^{\circ} 30'$  west of Tokio. During the eight years 1885–1892 the total number of earthquakes felt in the district was 3014, and of these 604, or 20 per cent., were accompanied by sound. The percentage, however, varies very widely in different parts of the area in question, and the continuous curves in fig. 2 represent this variation. Dividing the whole area into 56 rectangles, the sides of which are one-sixth of a degree of latitude and longitude in length, the percentage of audible earthquakes originating within each rectangle is supposed to correspond to the centre of that rectangle, and the curves are drawn in the same way as isacoustic lines. The meaning of any curve, say that marked 40, is as follows:—If any point on the curve be regarded as the centre of a small area, then 40 per cent. of the earthquakes whose centres are included within this area were accompanied by sound\*.

\* In constructing these curves the percentage was regarded as zero in the rectangles where there are no epicentres, or in isolated rectangles where the number of epicentres is *very* small.

The dotted lines in fig. 2 bound the area (incomplete towards the north) in which the destructive power of the earthquake was greatest; and within this area, again, the undulating line shows the path of the great fault-scarp of

Fig. 2.



more than forty miles in length. It will be noticed that the meizoseismal area is forked, the main branch proceeding towards the south, and that the principal group of curves follows this branch. The more northerly group of curves also lies along the main meizoseismal area, while the third group of curves lies roughly in the prolongation of the easterly branch of the meizoseismal area.

It will be seen in a later section that the sound in Japanese earthquakes is only heard within a few miles from the origin. Other conditions, then, being the same, it follows that superficial earthquakes would have a greater chance of being

audible than those which originate at a greater depth, and that the curves of highest percentages correspond to the earthquakes with the shallowest foci. It is therefore possible that the axes of the systems of curves in fig. 2 may mark out approximately the lines of growing faults.

#### *Relation between the Intensities of the Shock and Sound.*

Within and near the epicentral region of an earthquake, the intensity of the sound increases and decreases with that of the shock. Also, when the shock consists of two series of vibrations or contains two maxima of intensity, the stronger series or maximum is accompanied by the louder noise ; but the difference of intensity in the case of the sound is much less pronounced than in that of the shock.

In different earthquakes, again, while the intensities of the sound and shock certainly appear to increase together, the sound which accompanies the stronger shocks is not much louder than that which attends the weaker ones at places near the epicentre. Similar terms are used in describing both : in the one case, for instance, the rumbling of a train going over a bridge only intensified a hundred times ; in the other, the rumbling of thirty or forty waggons travelling at a rapid pace. Humboldt also notices that "the intensity of the hollow noise which generally accompanies an earthquake does not increase in the same degree as the force of the oscillations"\*. In the Comrie earthquakes, according to one observer, "a loud noise accompanies every shock, proportionate in loudness to its strength, . . . but in the lesser ones no vibration is perceptible, merely the peculiar report is heard." Again, in October 1846 three great shocks occurred in New Zealand, and were succeeded by numerous slight tremors. "In the two last of the three grand shocks," writes Sir W. Fitzherbert, "the roaring was certainly considerable, but it was inconsiderable when compared with the concussion, whilst in the minor shocks the vibration was trifling as compared with the report"†.

#### *Relations between the Sound-Area and the Disturbed Area.*

*Relative Magnitude of Sound-Area and Disturbed Area.—* The ratio which the extent of the sound-area bears to that of the disturbed area ranges continuously between the widest possible limits. At the one limit, the shock is felt but is unaccompanied by sound ; at the other, the sound is heard without any attendant shock.

\* *Cosmos* (Bohn's edition), vol. i. 1849, p. 203.

† Quoted by Sir J. Hector, Austral. Assoc. Trans. vol. iii. 1891, p. 523.

(1) The case in which no sound is heard has already been considered in discussing the inaudibility of some earthquakes ; and it is probable, as there suggested, that the absence of recorded sound is due to the defective auditory powers of the observers.

(2) In the great majority of strong and violent earthquakes, the sound-area occupies a region surrounding the epicentre, while the disturbed area extends beyond it in every direction. In Great Britain, the sound-area in our strongest earthquakes is often considerable. In the Pembroke earthquake of 1893, the disturbed area contains about 63,600 square miles and the sound-area about 37,700 square miles, being 231 miles long and 210 miles broad. The Hereford earthquake of 1896 disturbed an area of not less than 98,000 square miles, while the sound was heard over a district 320 and 284 miles in length and breadth and about 70,000 square miles in area. The Essex earthquake of 1884 was felt over about 50,000 square miles, and, excluding an isolated observation, the sound was heard as far as 114 miles from the centre \*.

Similar materials for the earthquakes of other countries are rare. In the Verny (Turkestan) earthquake of 1887, the disturbed area is about 950 miles long, 560 miles broad, and about 400,000 square miles in area ; the corresponding dimensions for the sound-area are 650 and 290 miles, and about 132,000 square miles †. The Neapolitan earthquake of 1857, according to Mallet, was felt over the whole Italian peninsula south of latitude 42° ; the sound-area was confined to the neighbourhood of the epicentre, and contained only 3300 square miles ‡. Of another Italian earthquake, that of March 12, 1873, the disturbed area measures approximately 670 and 430 miles in length and breadth, and 227,000 square miles in area ; excluding one isolated place (Fiume), the sound was heard over an area 236 miles long, 120 miles broad, and 22,000 square miles in area §. In the Charleston earthquake of 1886 the sound was heard at many places more than 700 miles from the origin, and also at three places in New Hampshire more than 800 miles ||.

\* R. Meldola and W. White, 'Report on the East Anglian Earthquake of April 22nd, 1884' (Macmillan, 1885).

† J. V. Mouchketow, 'Le Tremblement de Terre de Verny, 28 Mai (9 Juin), 1887,' *Mém. du Comité Géologique* (St. Pétersbourg, 1890). The above figures are obtained by measurement from the map accompanying this memoir.

‡ 'The Great Neapolitan Earthquake of 1857,' vol. ii, pp. 287-288.

§ These figures are deduced from records contained in A. Serpieri's 'Scritti di Sismologia,' parte i. 1888, pp. 44-97.

|| C. E. Dutton, U.S.A. Geol. Surv., Annual Rep., 9th Rep. pp. 411-528.

While the sound-area may thus attain such great dimensions in European and American earthquakes, the case is very different in those felt in Japan. When Prof. Milne remarks that "earthquake sounds only travel a few miles from their origin"\*, or "the very fact that the sound . . . was heard indicates . . . that those who heard the noise were not many miles removed from the origin"†, he is referring to his experience of Japanese earthquakes in the first instance, and probably relying on it in the second. With the detailed studies on which this conclusion is founded I am not acquainted, except in one case, that of the earthquake of February 22, 1880, in which the shock was sensible for a distance of 120 miles, while sound-records come as a rule from places not more than 14 miles from the epicentre ‡. More decisive evidence is, however, afforded by the percentage of audibility of the Japanese submarine earthquakes. In the earthquakes which originated beneath land, during the years 1885–1892, the percentage of those accompanied by sound is, as we have seen, 26·5. For the submarine shocks for the same period the percentage is only 0·84, and none of the earthquakes studied originated at a greater distance than 40 or 50 miles from the shore, while the epicentres of 93 per cent. of the total number were not more than 10 miles distant.

The comparatively poor powers of the Japanese people for hearing deep sounds are of course responsible for the small dimensions of the sound-areas. The limited sound-area of the Neapolitan earthquake is perhaps due to want of observations, Mallet's inquiries having been confined principally to the epicentral region. In the Charleston earthquake, we have a large sound-area with an apparently low percentage of audibility; but the smallness of the latter quantity is probably owing to the imperfection of the records, for the percentage in the central State of South Carolina is less than in six more distant States. For the more recent British earthquakes observations are numerous, and here we have a high percentage of audibility occurring with comparatively large sound-areas.

(3) In a few earthquakes the disturbed area and sound-area practically coincide, the boundaries of both being determined by the same places of observation. The shocks are generally of moderate strength, the disturbed areas ranging from about 400 to 2000 square miles, and in one case, that of the Inverness earthquake of 1890, to 4340 square miles.

\* *Japan Seismol. Journ.* vol. iv. 1895, p. xviii.

† 'Daily Telegraph,' Dec. 18, 1896.

‡ *Japan Seismol. Soc. Trans.* vol. i. pt. 2, 1880, pp. 53, 56–57, 105.

(4) In many slight British earthquakes the sound-area overlaps the disturbed area, as a rule only on one side, but sometimes in every direction. The Cornwall earthquake of April 1, 1898, had a disturbed area of about 175 square miles, beyond which the sound-area extended for a mile or two towards the south-west, north, and north-east (see fig. 3, p. 60). In the Comrie earthquake of July 12, 1895, the disturbed area contained only  $18\frac{1}{2}$  square miles ; the sound-area overlapped its boundary by two or three miles towards the north and west, if not in all directions. The Comrie earthquake of Aug. 26, 1898, was still weaker ; the sound-area contained but a few square miles, while the shock was only felt at one or two places within it.

(5) The limiting case, in which earth-sounds are heard without any accompanying shock, is of considerable interest. As a general rule, they appear to form part of the series of after-shocks of a great earthquake, or occur as intercalated members of a series of weak shocks. But it is possible that, under the names of barisal guns, mist-poeffers, marinas, &c., they may also be heard quite detached from an earthquake-series ; though the identification of these mysterious noises with earth-sounds must be regarded as uncertain for the present.

Most, if not all, great earthquakes appear to include numerous earth-sounds among their attendant crowds of after-shocks, especially in and near the epicentral regions. Even in Japan, where the audibility-percentage is so low, they are far from uncommon. For instance, the 3365 after-shocks of the Mino-Owari earthquake recorded at Gifu between Oct. 28, 1891, and the end of 1893, included 10 violent shocks, 97 strong, 1808 weak, 1041 feeble shocks, and 409 earth-sounds\*. On the other hand, in Great Britain, where the audibility-percentage is high, earth-sounds are occasionally numerous, especially at Comrie. After the strong shock of Oct. 23, 1839, one observer at Comrie noted between this date and the end of 1841, 19 earthquake-shocks (10 of which are described as vertical, and 7 lateral), 25 tremors, and 234 earth-sounds †.

It seems unnecessary to accumulate many further examples, but reference should be made to three cases in which earth-sounds were especially numerous. In the island of Meleda, in the Adriatic Sea, earth-sounds were heard during the

\* F. Omori, *Journ. Coll. Sci. Imp. Univ. Japan*, vol. vii. pt. 2, p. 113.

† J. Drummond, *Phil. Mag.* vol. xx., 1842, pp. 240-247. A similar series of earth-sounds followed the Comrie earthquake of March 12, 1795.

years 1822–1826. Partsch, in his valuable memoir describing them, inserts a chronicle of the shocks and sounds observed by a resident in the island, from Nov. 17, 1824, to Feb. 18, 1826; from which it appears that there were during this time 30 shocks and 71 detonations. Of the shocks, all but three were accompanied by sound; and 18 of the remaining shocks are described as “succussory,” i. e. they consisted of a more or less vertical movement\*.

The district surrounding East Haddam, in Connecticut, U.S.A., is another in which earth-sounds were at one time frequent. Before the English settlements, they were well known to the Indian inhabitants, who called the place *Morehemoodus*, or place of noises, and “drove a prodigious trade at worshipping the devil” there. The sounds are described in the following terms by a writer in 1729:—“Whether it be fire or air distressed in the subterraneous caverns of the earth, cannot be known; for there is no eruption, no explosion perceptible, but by sounds and tremors, which sometimes are very fearful and dreadful. I have myself heard eight or ten sounds successively, and imitating small arms, in the space of five minutes. I have, I suppose, heard several hundreds of them within twenty years; some more, some less terrible. Sometimes we have heard them almost every day, and great numbers of them in the space of a year. Oftentimes I have observed them to be coming down from the north imitating slow thunder, until the sound came near, or right under, and then there seemed to be a breaking, like the noise of a cannon shot, or severe thunder, which shakes the houses and all that is in them.” Another observer, writing about the beginning of the present, or end of the last century, says:—“The awful noises described in the preceding extract . . . . continue to the present time. The effects they produce are various as the intermediate degrees between the roar of a cannon and the noise of a pistol. The concussions of the earth, made at the same time, are as much diversified as the sounds in the air. The shock they give to a dwelling-house is the same as the falling of logs on the floor. The smaller shocks . . . . are spoken of as usual occurrences, and are called Moodus noises. But when they are so violent as to be heard in the adjacent houses, they are called earthquakes”†.

\* *Bericht über das Detonations Phänomen auf der Insel Meleda bey Ragusa* (Wien, 1826) pp. 204–211.

† Quoted by W. T. Brigham, Boston Soc. of Nat. Hist., Mem. vol. ii. 1871, pp. 14–16.

Lastly, a very remarkable series of earth-sounds is that described by Humboldt as the subterranean thunder of Guanaxuato, a city on the Mexican plateau far removed from any active volcano. "The noise," he says, "began about midnight on the 9th of January, 1784, and continued for a month . . . From the 13th to the 16th of January, it seemed to the inhabitants as if heavy clouds lay beneath their feet, from which issued alternate slow rolling sounds and short quick claps of thunder. The noise abated as gradually as it had begun. It was limited to a small space and was not heard in a basaltic district at a distance of a few miles." "Neither on the surface of the earth, nor in mines 1600 feet in depth was the slightest shock to be perceived. No similar noise had ever before been heard on the elevated table-land of Mexico, nor has this terrific phenomenon since occurred there" \*.

From the above examples, and from others that might be quoted, we may infer : (1) that earth-sounds especially characterize those districts where slight shocks are frequent ; (2) that in the midst of a series of earth-sounds one or more slight shocks, accompanied by precisely similar sounds, are occasionally intercalated †; (3) that when moderate shocks are felt, the earth-sounds are heard at places where the motion is frequently vertical, and, when strong shocks are felt, at places within the epicentral districts ; and (4) that in any one district, that of Comrie for example, there is a complete continuity from earthquake to earth-sound ; every stage of the process is before us, from the strong earthquake in which the disturbed area extends in all directions beyond the sound-area, through the weak earthquake, in which the relations of the areas are reversed, down to the earth-sound, when the shock itself is imperceptible. We may therefore conclude that earthquakes and earth-sounds are manifestations, differing

\* *Cosmos* (Bohn's edition), vol. i. pp. 203, 205-6.

† It is worthy of notice that the sound in these cases is generally of short duration. For instance, the earth-sounds following the Comrie earthquake of 1839 are described by Drummond as "gas explosions." Prof. Omori also remarks (*Journ. Coll. Sci. Imp. Univ. Japan*, vol. vii. pt. 2, 1894, pp. 197-198) that "many of the after-shocks of the Mino-Owari earthquake were attended with sounds, which were essentially of two types, being either rushing feeble noises like those caused by winds, or loud rumbling sounds like those caused by the fall of a heavy weight on the ground, or by the discharge of a gun. The sounds of the second type, which were sometimes like detonations of thunder, were most frequent and distinct in the Neo Valley [the epicentral district], where, as I believe, their origin really was. It is remarkable that tremblings of the ground accompanying these sounds were invariably very feeble, and often not to be felt at all."

only in degree and in the method in which we perceive them, of one and the same phenomenon.

*Relative Position of Sound-Area and Disturbed Area.*—The excentricity of the sound-area with respect to the isoseismal lines is one of the most significant phenomena of earthquake-sounds. In weak earthquakes the sound is a more prominent feature than the shock, and it is in these that the excentricity is most easily detected; but I believe that, with a sufficiently careful study, it would be found to exist in nearly all earthquakes. Thus, in the Leicester earthquake of 1893, which disturbed an area 58 miles long from W.  $38^{\circ}$  N. to E.  $38^{\circ}$  S., and 46 miles broad, the sound-area and disturbed area apparently coincided. Near the north-west end of the longer axis, however, the shock was felt, but no sound was heard, by observers at five places; while at seven places towards the opposite end, the sound was heard without any shock being sensible. It is thus clear that the isacoustic lines, if they could have been drawn, would, relatively to the isoseismals, be displaced towards the south-east.

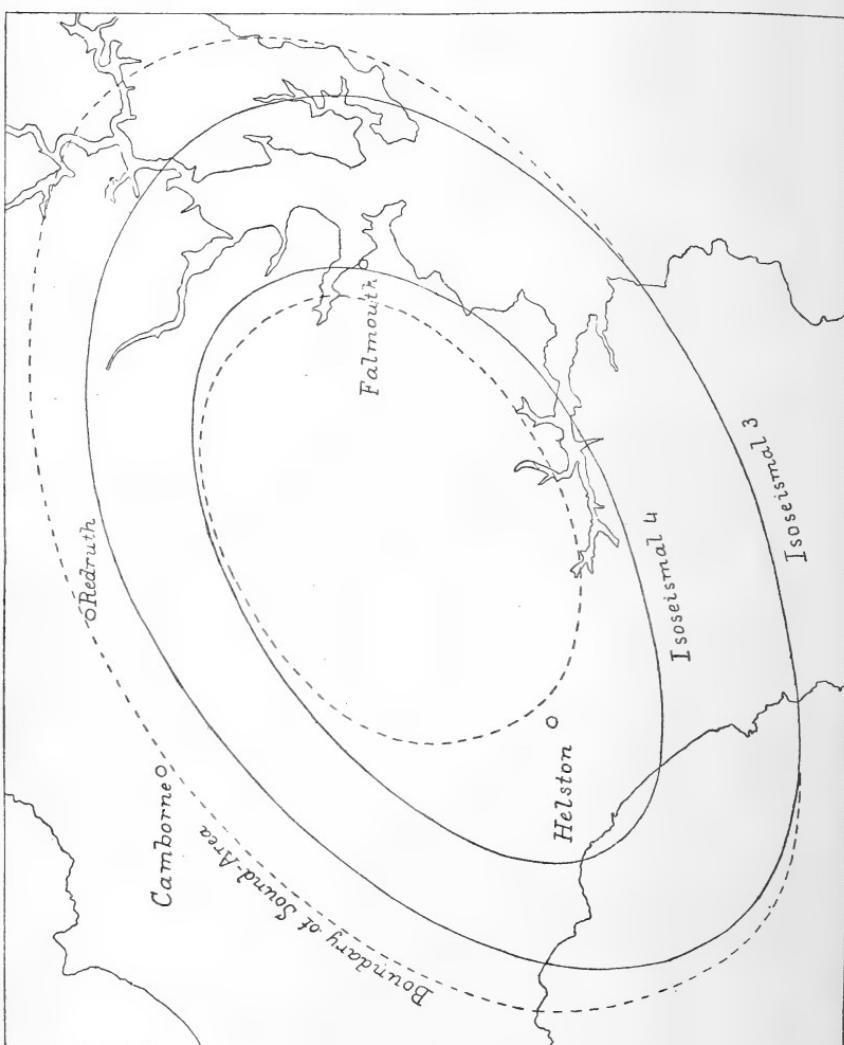
The sound-area of the Pembroke earthquake of 1893 was bounded by a line similar in form and size to the isoseismal 4, such that, if the latter curve were shifted about ten or twelve miles in the direction of its longer axis, it would roughly coincide with the former line. In the Neapolitan earthquake of 1857, the records collected by Mallet in his great work show that the boundary of the sound-area is similarly displaced in the direction of the longer axis of the innermost isoseismal. The peculiar form of the isacoustic lines of the Hereford earthquake of 1896 and their aberration from the isoseismal lines have been alluded to above. The observations of the Edinburgh and Lancashire earthquakes of 1889 are somewhat scanty, but they appear to indicate that the sound-areas were shifted towards the lines of the earthquake-faults \*.

In the slight earthquakes of this country the excentricity of the sound-area is manifested by its overlapping the disturbed area in one direction. In the accompanying map (p. 60) the continuous lines represent the isoseismals of intensities 3 and 4 of the Cornwall earthquake of April 1, 1898. The outer dotted line indicates roughly the boundary of the sound-area, and the inner dotted line, which is concentric with the former, separates the places where the sound was very loud from those where it was distinctly fainter. The relative positions of the isoseismals show that the earthquake-fault must have had towards the south-east, and therefore that the sound-area,

\* Geol. Mag. vol. viii. 1891, pp. 64, 311.

relatively to the disturbed area, is displaced towards the line of fault.

Fig. 3.



#### *Place of Earth-Sounds in an Earthquake-Series.*

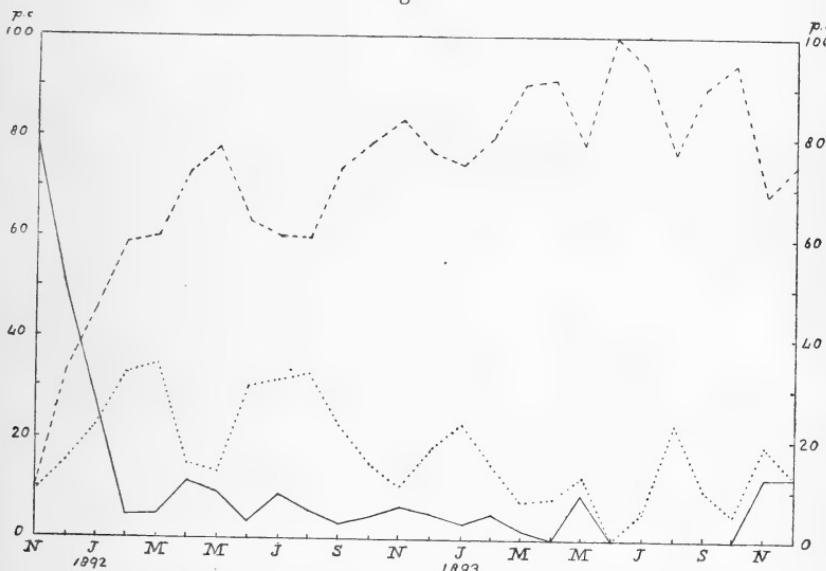
In an admirable memoir, Prof. Omori has shown how the after-shocks of a great earthquake are subject to a gradual but fluctuating decline in frequency and average intensity\*. At first sight, it might appear that earth-sounds which, as we have seen, are merely earthquakes too weak to be felt, should be relatively more frequent towards the end of an

\* "On the After-Shocks of Earthquakes," Journ. Coll. Sci. Imp. Univ. Japan, vol. vii. pt. 2, pp. 111-200.

earthquake-series. But this does not seem to be the case, so far as we can judge from the limited materials at our disposal.

The series of the Mino-Owari after-shocks recorded at Gifu is the most valuable and complete of any so far published. Prof. Omori gives the number of earthquakes for every day from Oct. 28, 1891, to Dec. 31, 1893, classifying them under the heads violent shocks, strong shocks, weak shocks, feeble shocks, and sounds. From this catalogue the curves in fig. 4 have been constructed. Those for the violent and

Fig. 4.



strong shocks have been omitted, on account of their numerical inferiority. The three curves, continuous, broken, and dotted, represent respectively the percentages (with regard to the total number of earthquakes each month) of the weak shocks, feeble shocks, and sounds, beginning in Nov. 1891. During the first three months, the weak shocks rapidly decline in relative frequency, while there is a corresponding increase in that of both feeble shocks and sounds. But, at the end of five months, the two latter curves begin to diverge, the feeble shocks being subject to a fluctuating increase, and the sounds to a fluctuating decrease, in relative frequency.

Very similar, though less exact, is the evidence furnished by Drummond's Comrie record from Oct. 1839 to Dec. 1841, the principal shock being that which occurred on Oct. 23, 1839 \*. In this series the earth-sounds greatly predominated,

\* Phil. Mag. vol. xx. 1842, pp. 240-247.

there being 276 earth-sounds and only 54 shocks and tremors. If we divide the whole time into nine intervals of three months each, the percentages of earth-sounds in the several intervals are 87, 89, 88, 100, 95, 80, 50, 76, and 50; showing that towards the close of the period considered, the perceptible shocks increased in relative frequency.

#### *Time-Relations of the Sound and Shock.*

In earthquake-catalogues, the time-relations of the sound and shock are not often recorded; and it is therefore probable that such entries, when they do occur, refer to the more prominent relations. In Mallet's great catalogue, for instance, the time-relations are given for only 423 earthquakes; and in these the sound is said to have preceded the shock in 100 cases, accompanied it in 307, followed it in 9, preceded and accompanied it in 2, accompanied and followed it in 2, and preceded, accompanied, and followed it in 3 cases. Thus, either the sound occurred more frequently before the shock than after, or the sound which preceded the shock was louder and more readily observed than that which followed.

In studying the more recent British earthquakes, I have endeavoured to attain greater precision in defining the time-relations of the three principal epochs of the sound and shock, namely, the beginning, epoch of maximum intensity, and the end. In the Table which follows, the letters *p*, *c*, and *f* indicate the number of records in which any epoch of the sound preceded, coincided with, and followed the corresponding epoch of the shock. The first five shocks were all weak.

TABLE VI.

Earthquake.	Beginning.			Epoch of Maximum Intensity.			End.		
	<i>p.</i>	<i>c.</i>	<i>f.</i>	<i>p.</i>	<i>c.</i>	<i>f.</i>	<i>p.</i>	<i>c.</i>	<i>f.</i>
Cornwall, 1892 .....	12	3	1	...	...	...	1	5	8
" 1895 .....	1	4	...	...	1	...	...	2	1
" 1896 .....	4	...	...	...	...	..	...	1	...
" 1898 .....	5	4	...	...	2	...	...	4	2
Exmoor, 1894 .....	9	...	...	...	6	...	...	1	4
Leicester, 1893 .....	59	11	3	19	18	3	16	6	16
Pembroke, 1892 .....	84	35	13	19	56	5	14	17	73
" 1893 .....	80	16	15	9	32	9	7	11	55
Hereford, 1896 .....	503	71	39	25	85	7	72	88	161
Percentage for each epoch, weaker shocks .....	72.1	25.6	2.3	...	100.0	...	3.5	44.8	51.7
Ditto, stronger shocks .....	78.1	14.3	7.5	25.1	66.6	8.4	20.3	22.8	56.9

Thus, as a general rule, the beginning of the sound precedes that of the shock, but occasionally coincides with it, especially when the earthquake is weak. For weak shocks the epochs of maximum intensity of both always coincide ; while, for stronger shocks, the epoch of maximum intensity of the sound generally coincides with, but sometimes precedes, that of the shock. The end of the sound hardly ever precedes, but often coincides with, that of the shock in weak earthquakes, and in both strong and weak earthquakes more frequently follows it than otherwise.

*Time-Relations with regard to Distance from the Epicentre.*—The great majority of the records are from places not far from the epicentre. The effect of distance on the time-relations is shown more clearly in the next Table (p. 64), in which the number of observations is given for each epoch and district ; but for convenience of comparison the figures in the other columns are percentages of the numbers of observations. This Table of necessity refers only to the stronger earthquakes.

It appears, then, that the beginning of the sound generally precedes that of the shock in all parts of the sound-areas, even close to the epicentre.

The epochs of maximum intensity of the sound and shock coincide, as a rule, especially in the central counties and outer ring ; but in the inner ring of counties observations of precedence increase in frequency. In the case of the Hereford earthquake, an analysis of the observations according to direction, though it rests on a small number of records, indicates that the percentage of observations of coincidence undergoes a marked decrease in the inner ring in the counties traversed by the longer axis of the isoseismal lines, while in those which lie along the shorter axis it is nearly constant. The much weaker Leicester earthquake of 1893 leads to a somewhat similar conclusion. The epoch of maximum intensity of the sound preceded that of the shock at 19 places, which are, as a rule, near the ends of the longer axis of the disturbed area ; and coincided with it at 18 places, which are not far distant from the epicentre or shorter axis, and in two cases close to the ends of that axis.

In the Pembroke earthquake of 1892, the end of the sound generally followed that of the shock all over the disturbed area ; in that of 1893, observations of coincidence increase with the distance from the origin. On the whole, the percentages for this epoch in the Hereford earthquake do not vary much with the distance. In the Leicester earthquake of 1893 the end of the sound preceded that of the shock at 16 places generally near the longer axis of the disturbed area, and

TABLE VII.

Earthquake and District.	Beginning.				Epoch of Max. Int.				End.			
	No. of Obs.	p.	c.	f.	No. of Obs.	p.	c.	f.	No. of Obs.	p.	c.	f.
Pembroke, 1892.	87	49	45	6	70	16	76	8	79	9	15	76
	30	87	7	7	12	25	67	8	12	8	25	67
	27	63	11	26	6	17	67	17	14	14	14	71
Pembroke, 1893.	80	75	12	12	40	12	70	17	52	2	12	86
	13	62	23	15	5	0	60	40	6	17	17	67
	30	60	27	13	7	43	57	0	18	11	50	39
Herrford, 1896.	303	84	11	5	80	19	79	2	158	22	29	49
	187	80	13	7	18	44	44	11	102	24	24	51
	154	82	9	9	18	.....	78	22	75	20	24	56
Aldridge, the Axes, 1896.	76	85	10	4	23	9	91	.....	41	24	24	51
	37	76	22	3	6	67	17	17	19	37	37	26
	22	73	14	14	7	.....	86	14	13	23	23	54
Herrford, 1896. Perpendic. to the Axes.	67	86	6	7	15	33	67	.....	35	31	31	37
	112	83	8	9	5	20	60	20	60	60	23	58
	27	82	7	11	3	.....	67	33	8	37	25	37

especially close to the ends of it; and it followed it at 16 places chiefly near the epicentre or the shorter axis.

*Apparent Outracing of the Shock by the Sound.*—The partial coincidence of the sound with the shock at places near the epicentre, and its precedence at others more distant, have led some seismologists to believe that the sound-vibrations travel with a greater velocity than those which constitute the perceptible shock\*. From the evidence of British earthquakes we may conclude that the difference in velocity, if it exist, is very slight; for, otherwise, the sound could not be heard after the shock at places so far distant as 180 miles from the epicentre†.

In the earthquakes of some other countries it would seem that the sound generally ceases before the shock, and often before the shock begins. In such cases there is clearly at least an apparent outracing of the shock by the sound; but it is not improbable that this is due merely to the defective powers of the observers for hearing the weak sound which follows the shock.

*Relative Duration of the Sound and Shock.*—When the time-relations of both beginning and end of the sound and shock are noted by observers, it is generally possible to determine their relative duration. The figures in the following table give the number of records in which the duration of the sound is greater than, equal to, or less than that of the shock, as well as the number in which the relative duration is doubtful.

The most important figures in Table VIII. (p. 66) are those which give the duration of the sound as greater or less than that of the shock. Those which make the duration of both equal are not entitled to the same consideration; for the statement that the sound and shock were coincident at both ends is less precise than the others. We may therefore conclude that the duration of the sound is generally greater than that of the shock.

\* For instance, J. Drummond, Phil. Mag. vol. xx. (1842) p. 240; E. J. Lowe, Proc. British Meteor. Soc. vol. ii. (1865) p. 55; H. J. Johnston-Lavis, Geol. Mag. vol. ix. (1892) pp. 280-281; T. Taramelli and G. Mercalli, *R. Accad. dei Lincei, Memorie, &c.*, vol. iii. (1885) p. 55, and *Annali dell' Uff. Centr. di Meteor. e Geod.* vol. viii. (1888), parte iv.; M. Baratta, *ibid.* vol. iii. (1889) parte iii.

† As at Baltinglass (co. Wicklow) in the Hereford earthquake of 1896.

TABLE VIII.

Earthquake.	Duration of Sound with reference to that of Shock.			
	Greater.	Equal.	Less.	Doubtful.
Cornwall, 1892 .....	5	1	...	1
,, 1898 .....	2	3	...	...
Exmoor, 1894 .....	5	...	...	...
Leicester, 1893 .....	22	8	1	6
Pembroke, 1892.....	69	11	4	8
,, 1893 .....	49	11	4	6
Hereford, 1896 .....	86	40	12	63
Total .....	238	74	21	84
Percentage .....	57	18	5	20

*Origin of Earthquake-Sounds.*

In any earthquake there are generally three well-defined stages of motion—the preliminary tremor, the principal portion, and the end portion. In the first, the characteristic movements are small in amplitude and short in period; the second and most active part of the disturbance consists chiefly of vibrations of larger amplitude and longer period; and these are followed by the feeble movements which constitute the end portion. Slow undulations, with a period of about one-half to two seconds, may, however, be present in all three stages; while the ripples, with a period of one-tenth of a second or more, may be superposed on the slow undulations in the second and third stages as well as in the first. The average period of the ripples, it is important to notice, is slightly greater during the principal portion than during the other two stages\*.

During the earlier part of the movement there is a distinct increase in the period of the vibrations; and this has led some seismologists † (all at the time living in Japan) to suggest

\* See a valuable paper by F. Omori and K. Hirata, "Earthquake Measurement at Miyako," Journ. Coll. Sci. Imp. Univ., Tokyo, vol. xi. (1890) pp. 161-195.

† J. A. Ewing, "Earthquake Measurement," Mem. of the Sci. Department, Univ. of Tokio, No. 9 (1883), p. 11; J. Milne, Japan. Seismol. Soc. Trans. vol. xii. (1888) pp. 58-59; F. Omori, Journ. Sci. Coll. Imp. Univ., Tokyo, vol. xi. (1890) p. 147.

that the first recorded tremors may be the successors of those which produce the preliminary earthquake-sound. The observations of British earthquakes show, however, that the sound-vibrations are not confined to the earlier stage, but that, like the ripples, they are also superposed on the slow undulations which form the main feature of the principal and end portions of an earthquake.

Some of the phenomena of earthquake-sounds, as we have seen, are due to the neighbourhood of the sound to the varying lower limit of audibility. There are others, such as the time- and space-relations of the sound and shock, for which a different explanation is required, and whose origin is of a geological rather than a physical character.

The theory which follows is based on the supposition that the majority of non-volcanic earthquakes are due to the gradual, but intermittent, growth of faults; the immediate cause of the disturbance being the friction produced by the slipping and rubbing of one of the adjoining rock-masses over and against the other\*.

A fault-slip does not of necessity take place concurrently all over the focus or instantaneously at any one point of it. But, as a general rule, it certainly occupies a very short interval of time, and at places near the epicentre the duration of the sensible part of an earthquake must be mainly due to the size of the focus and the finite velocity of the earth-waves.

The seismic focus is practically a surface inclined to the horizon, and is often of great length in a horizontal direction. In its simplest form there will be a central region of the fault-surface where the relative displacement of the two rock-masses is a maximum, and this will be surrounded by a region in which the relative displacement is small, and gradually dies away towards the edges. As the vibrations of great amplitude are also of long period, we may consider that from all parts of the focus there start together vibrations of various amplitude and period, the large and slow undulations coming mostly from the central region, and the small and rapid vibrations from those which bound it. It is, I believe, from these

\* The principal facts in favour of the fault-slip theory are:—(1) The elongated forms of the isoseismal lines, the longer axes of which in any district are, as a rule, either parallel or perpendicular to one another, and parallel, or nearly so, to the chief lines of fault; (2) the formation of fault-scarsps concurrently with violent earthquakes; (3) the impossibility of a great fault growing otherwise than by an almost infinite number of slips; and (4) the enormous excess of the number of earthquakes over the number of faults in any one district.

marginal regions, and especially from the upper and lateral margins, that the more sensible sound-vibrations chiefly come. I will now endeavour to show how the phenomena of earthquake-sounds can be explained on this theory.

If there is no discontinuity in period between the large vibrations which come from the centre of the area and the sound-vibrations from the focal margins, it is evident that among the vibrations must be included those which produce the deepest sound that can be heard by the human ear. The rumbling character of the sound may be due partly to its neighbourhood to the lower limit of audibility, partly, no doubt, to irregularities in the fault-surface producing local variations in the initial disturbance. To the latter cause may also be owing the intermittent sounds heard by some observers.

But whether there be any slight fluctuations in amplitude and period, or not, it is evident that the average intensity of the sound must gradually increase until the shock is felt; and as soon as it is over, or nearly over, must gradually die away. At the same time the greater amplitude of the vibrations from near the central part of the focus will render audible vibrations of longer period than those which come from the margins; and thus the depth of the sound will increase and decrease with the intensities of the sound and shock. Especially will this be the case with the vibrations from the neighbourhood of that part of the focus where the initial amplitude is greatest; and the strongest vibrations and loud explosive crashes audible to some persons should therefore be observed concurrently.

Similar reasoning leads to the conclusion that the intensity of the sound should increase with that of the shock in different earthquakes, and that the sound should be deeper with strong shocks than with weak ones. But while the marginal vibrations are limited in period and amplitude, those from the central parts of the focus have a much wider range. With very weak shocks the sound should be the most prominent feature; with very strong ones the sound, though actually louder, should be relatively insignificant; and when, as in the Hereford earthquake, the earthquake consists of two distinct parts, the two shocks may differ widely in intensity, while the accompanying sounds may be almost equally loud.

With observers of given average auditory powers, the magnitude of the sound-area depends on the limited strength of the marginal vibrations, and on the dimensions of the seismic focus, and therefore of its marginal regions. The magnitude of the disturbed area depends partly on the size of the focus,

chiefly perhaps on the initial intensity of the vibrations from its central portion. While the dimensions of the sound-area should generally increase with those of the disturbed area, it is evident that they should not increase in the same ratio. With very strong shocks, the sound-area should be a comparatively small district surrounding the epicentre. With very slight ones, the marginal regions would be so great compared with the central portion of the focus, that the sound-area might overlap the disturbed area. In the limit, the central portion of the focus would vanish, and an earth-sound would be the only result sensible to human beings\*.

Several of the phenomena of earthquake-sounds depend on the superficial form and inclined position of the focus, and on the fact that the most sensible sound-vibrations come from the upper and lateral margins. The isacoustic lines and the boundary of the sound-area should not be concentric with the isoseismal lines. Relatively to the latter the sound-area will be shifted towards the fault-line, and also in a direction parallel to it, if one lateral margin should predominate over the other.

The time-relations of the sound and shock remain to be considered. The sound-vibrations from the margin nearest to the observer should be heard before the shock begins, those from the upper margin, and possibly from parts of the central portion, during the progress of the shock, and those from the furthest margin after the shock ends. Moreover, the sound-vibrations from the nearer lateral margin will be of greater intensity than those from the further one; and thus the fore-sound should be more generally heard than the after-sound, and with Japanese and some other observers should be the only one perceptible. The percentage of observations of the after-sound should also diminish with the increasing distance from the origin; and the duration of the sound, especially near the epicentre, should be greater than that of the shock.

At places near the epicentre, and also at places whose distances are great compared with the dimensions of the focus, the sound-vibrations which appear loudest will be those which originate near the central portions of the focus; and thus the epochs of maximum intensity of the sound and shock should coincide. If, however, the horizontal length of the nearer focal margin be considerable, the sound which seems loudest to observers at a moderate distance may come from or

\* It has been suggested that the comparative smallness of the sound-area may be due to the more rapid extinction of the sound-vibrations; but the explanation is clearly incomplete, for it fails in the cases in which the sound-area overlaps the disturbed area.

near that margin ; for there is but little change in the initial intensity of the sound-vibrations from the neighbourhood of the central portion. To observers who are situated near the continuation of the line of fault, the maximum epoch of the sound will therefore precede that of the shock ; while to those who are near the minor axis of the isoseismals, the two epochs will approximately coincide.

#### IV. *Contact Electricity*.

*By FREDERICK S. SPIERS, B.Sc., A.C.G.I.\**

§ 1. **T**HE object of this investigation was to determine, in a more satisfactory manner than has hitherto been attempted, the part that the medium plays in the P.D. that is observed between two dissimilar metals when they are metallically connected. No experiment on this important point, whether made *in vacuo* or in any gas whatsoever, can be considered decisive unless the films of air condensed on the two plates of metal be first removed. If the Volta effect is due to the air at all, it is most certainly due to that part of the atmosphere immediately surrounding the metals, namely, to the condensed surface-layers of air or oxygen ; and hence it is in the highest degree essential to be certain of the entire removal of this surface-layer before any experiments can be considered decisive. The molecular attraction between a metal and the gaseous film in close contact with it is probably of very considerable magnitude ; hence it is useless simply to surround the metals with another gas, and then assume that your measurements are being made in that second gas, ignoring the original condensed sheet of air.

Most experimenters on the subject have either ignored altogether or else failed to realize in full the presence and possible action of these air-sheets condensed on the metals. A critical and, I may add, wholly delightful account of the work done prior to the year 1884 is to be found in the exhaustive report presented by Prof. Oliver Lodge to the British Association in that year. Nobody will venture to claim finality for any experiment bearing on the subject that is described in that report. Neither can it be said that any work published since that date effectually and decisively clears up the many doubts and difficulties with which this matter bristles. There are, however, two important researches concerning which a few remarks here would not be out of place.

\* Communicated by the Physical Society : read Nov. 10th, 1899.

One of these is by Dr. J. T. Bottomley, F.R.S.\* and the other by Dr. J. Erskine-Murray, F.R.S.E.† Dr. Bottomley merely measured the Volta contact-difference between two disks of zinc and copper in high vacua of air and hydrogen, the pressure being less than  $\frac{1}{523}$  mm. of mercury, and showed that on readmitting air to atmospheric pressure no variation of the P.D. as great as 1 per cent. ensued. Seeing that Dr. Bottomley did not so much as warm his vacuum-tube, there is not much reason to suppose that the result would have been otherwise than what it actually was. Dr. Erskine-Murray, who quite realized the possible importance of the condensed air-films in the production of the Volta phenomena, attacked the problem rather more indirectly; but his method of removing the films by filing the surfaces of the metals under melted paraffin-wax cannot, I think, be considered as entirely satisfactory. In the first place it ignores the probable electrolytic action of the wax, or of the moisture in the wax, for apparently no precautions were taken to dry it; and even if these effects be disregarded, I believe it improbable in the highest degree that merely filing off the surface-layer of metal is sufficient to remove these condensed air-sheets. Why, the file itself is covered with a film of air!

§ 2. It seemed, therefore, that in spite of the enormous quantity of experimental work that this controversy concerning the contact effect had brought forth, there was still room for a crucial and decisive experiment which should go to the very root of the matter, and finally satisfy all conflicting parties. It was with this ideal, possibly unattainable like all true ideals, in view, that I began experiments in this field some two years ago.

§ 3. I will now proceed to describe in detail the various forms of apparatus that were devised for these investigations, and give a short account of the experiments that were made with each. As a rule, only the outlines and results of each experiment will be given; consequently but a small proportion of all the observations taken will be recorded here.

§ 4. Some preliminary experiments were made with the apparatus sketched in fig. 1, which was made for Profs. Ayrton and Perry about twenty years ago. In this they adopted the same principle as that used by them in the exhaustive series of contact E.M.F. measurements they made in Japan‡. In the figure A and B represent the contact-couple, in this case zinc and platinum. They are metallically con-

\* B. A. Report, 1885.

† Proc. Roy. Soc. 1898, vol. lxiii. p. 113.

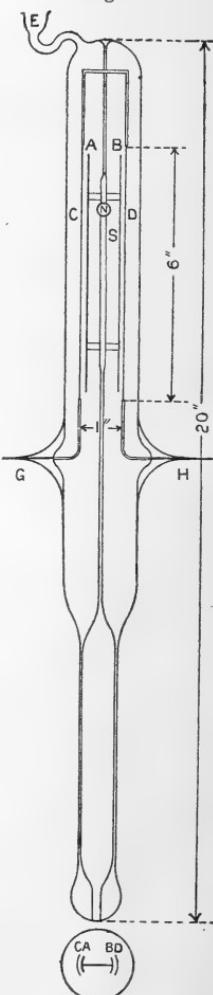
‡ See Proc. Roy. Soc. 1877 & 1878; Phil. Trans. 1880.

nected through the brass spindle S, with which they can revolve, there being a small magnet, N, fixed in the spindle which can be pulled round by an external horseshoe-magnet revolving on a turntable. C and D are two inductors of platinum rigidly fixed, top and bottom, in glass supports. In consequence of the Volta force, A and B are at different potentials, real or apparent. If now C and D be connected to the respective terminals of a quadrant-electrometer, brought to the same potential, and then one of them insulated and A-B turned through  $180^\circ$ , there will be a P.D. induced between C and D which, *ceteris paribus*, is proportional to the contact P.D. between A and B. (See Ayrton and Perry's papers quoted above.) The tube could be connected to a sprengel-pump by means of an india-rubber covered joint in the cup E, sealed in mercury.

The results obtained were not very satisfactory. The apparatus had been lying about in dusty cupboards for many years with the opening unclosed, so that the insulating-power of the glass supports was anything but high. In consequence of the small capacity of the system, quite a small amount of leakage caused a large change in the potential of the insulated inductor; and it is quite possible that the paraffin-wax in which the terminals G, H were sealed was not a sufficiently good insulator for this purpose. It was not possible to measure the absolute value of the Volta P.D. between A and B, as the two metals were in permanent metallic contact inside the tube; one could only measure any relative changes that took place in that value.

Several readings were taken in very high vacua, from about  $\frac{1}{5000}$  mm. of mercury pressure and upwards (as measured on a McLeod gauge), and a decrease of about 2 or 3 per cent. was observed in the deflexion when the tube was exhausted, the original value returning in each case when air was readmitted into the apparatus. In consequence of the vagueness of the

Fig. 1.



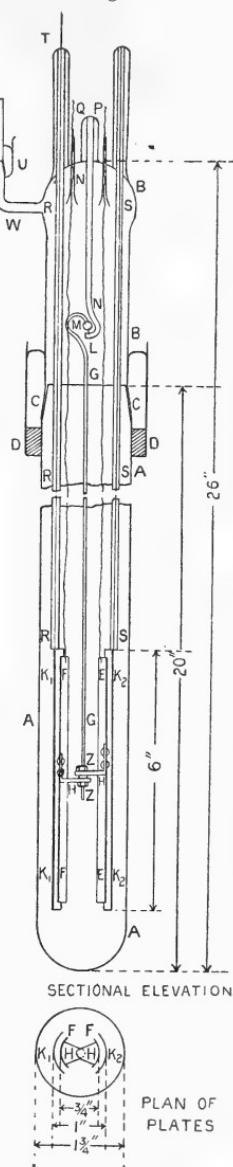
readings, however, not much stress must be laid on these results.

§ 5. In designing a new apparatus, the following points were specially kept in view:—(1) The desirability of being able to measure the actual value of the Volta effect. (2) The absolute necessity of being able to heat strongly the contact couple in the highest attainable vacuum. (3) The necessity of having high insulation, in consequence of the small capacities dealt with. It will be found subsequently that the exigencies of (2) reduced the capacity still further than would otherwise have been the case.

To fulfil condition (2) it was necessary to make the apparatus of hard combustion-tubing; but as such glass is extremely difficult to work, and as it would have been exceedingly troublesome, if not impossible, to seal glass tubes or platinum wires into it, it was decided to make the apparatus in two parts. This had the further advantage that the plates could be taken out and examined whenever desirable, which would not have been the case had the tube been entirely sealed up.

The apparatus is shown in fig. 2. A, A the lower half of the tube is made of the hardest combustion-tubing  $1\frac{3}{4}$  in. in diameter. It fits into the upper portion B, B, made of softer tubing, at the very carefully-ground glass joint C. The joint is sealed in mercury contained in a glass vessel, which slips over the rubber ring D. The two dissimilar metals E and F form the contact couple. Their dimensions are  $\frac{3}{4}$  in. by  $5\frac{3}{4}$  in. They are attached to the aluminium spindle G by means of the zinc lugs H, H, to which they are screwed. The spindle passes through slits in these lugs, and they are

Fig. 2.



kept tightly in place by means of the small nuts Z, Z which screw on to G. The nuts are insulated from the bolts and shaft and from one another with strips of mica. The spindle G is mounted at L on a needle-point that rests in a small hole in the glass support N, which is shaped as shown in the figure. M is the end view of a small bar-magnet which is screwed on the spindle. By means of an outside horseshoe-magnet revolving on a turntable one is able to turn M, and therefore the contact couple, through an arc of  $180^\circ$ , just as in the apparatus described in § 4.

Two very fine platinum wires are connected to the dissimilar metals E and F and pass out of the top of the glass tube through the seals at P and Q \*. K<sub>1</sub>, K<sub>2</sub> are the platinum inductors (each  $\frac{7}{8}$  in. by  $5\frac{3}{4}$  in.). These are bent into arcs of circles as shown in the plan of fig. 2, and sealed into the highly insulating glass tubes R and S. Platinum wires running through these tubes pass from the inductors K<sub>1</sub>, K<sub>2</sub> to the outside of the apparatus, into which they are sealed. The wire which was always kept earthed is sealed at T, as shown in fig. 2. In the case of the insulated one S, it was necessary to prolong the glass tube as shown in fig. 3 (S, S), so that a couple of inches of its surface could always be kept highly insulating by the common device of slipping on it a small flask containing a little strong sulphuric acid (T, fig. 3). The cork (U) is just slipped upwards when readings are being taken. This flask is not shown in fig. 2, as it would there appear in front of the apparatus instead of at the side, as in fig. 3. The outlet W (fig. 2) served to connect the tube to the air-pump. U is a ground-glass joint sealed in mercury.

§ 6. The method employed of measuring the contact P.D. between E and F was a combination of Ayrton and Perry's method (described in § 4) and the well-known compensation method used by Lord Kelvin †. The plates E and F were connected through the platinum wires ending at P and Q to two points on a potentiometer. The one inductor K<sub>1</sub> was joined to the earthed quadrants of the electrometer, the other K<sub>2</sub> to the insulated quadrants. The variable potentiometer contact was then adjusted until, on insulating K<sub>2</sub> and reversing the contact couple by means of the outside horseshoe-magnet, no deflexion of the electrometer needle took place. When this stage was reached the impressed P.D. from the potentiometer

\* It was an operation of some difficulty, even to the practised glass-blower, to make so many seals into one small piece of glass.

† B. A. Report, 1880, and 'Nature,' April 14th, 1881, also Dr. Lodge's Report B. A. 1885.

meter exactly counterbalanced the Volta E.M.F. between the plates E and F. A voltmeter gave the reading directly.

§ 7. The method of heating the lower part of the tube was to slip over it a tube of copper lined with asbestos. It was then found quite possible to bring the tube safely to a bright red heat with a blowpipe flame. The large distance between the source of heat and the upper part of the tube, only about 6 or 8 inches of the lower part being heated directly, prevented the joints and seals from becoming unduly heated, and conveyance of heat by convective air-currents was prevented by suitably placed sheets of asbestos cloth. It was at first feared that a large ground-glass joint such as C, C (fig. 2) would not be sufficiently air-tight for the very high vacua that it was desired to work with, but the joint proved to have been so very carefully ground \* that when scrupulously clean it would readily hold a vacuum as high as  $\frac{1}{10,000}$  mm., which was almost the limiting reading reliably given by the McLeod gauge. I always found that I could get a far better fit, although, on the other hand, it was then far more difficult to open after exhaustion, when the joint was quite clean and dry than when it was smeared with even a slight trace of glycerine.

In other respects the apparatus did not prove so satisfactory. In the first place it was necessary that the fine platinum wires attached to the movable plates E and F should be so flexible as not to exercise any appreciable control on the free motion of the system. On the other hand, if they were too loose there was fear of one or other of them coming into contact with the platinum inductors at some position through which it passed. It proved an exceedingly troublesome operation to make the exact adjustment of length necessary, and even at their best the wires always exercised a certain amount of control, so that it was never possible to revolve the moving system completely through  $180^\circ$  of arc. This, of course, materially diminished the sensibility of the arrangement. There was another cause which operated still more in reducing the sensibility, and that was the comparatively large distance between the movable plates and the inductors. This was in consequence of the necessarily great length of the spindle G, G, so that when the plates were closer than about  $\frac{3}{16}$  in., quite a small amount of side play caused by pulling round the system was sufficient to bring the plates into contact.

\* I might mention that the glass-blowing required in all these pieces of apparatus was most satisfactorily performed by Mr. C. E. Müller.

When the apparatus was working at its best, and the various adjustments were made with the utmost possible care, a P.D. between the movable plates E and F of one volt caused a deflexion on the electrometer of about 20 scale-divisions, the sensibility of the electrometer being such that a P.D. of a volt applied directly between its terminals gave a deflexion of 470 scale-divisions.

It was impossible to increase the size of the plate and thus augment the sensibility of the apparatus, because its dimensions were strictly limited by the diameter of the combustion-tubing (A, A, fig. 2). I was fortunate enough to get hold of a length of  $1\frac{3}{4}$  in. diameter. As far as I am aware there was not another piece of combustion-tubing in London of greater, or even as great, diameter.

§ 8. In the first experiments that were made with this apparatus the dissimilar metals were platinum and zinc. The P.D. between the two, after cleaning the latter with emery-paper and wiping with clean dry silk, was about 0·95 volt. To make measurements in high vacua I first exhausted the tube to a vacuum of about  $\frac{1}{2000}$  mm. (this took about four hours to obtain), without applying any heat at all. This caused no appreciable reduction of the contact force. (In these experiments the degree of accuracy is not greater than 0·05 of a volt.) The tube was then gently heated with a single bunsen-flame, and the pressure soon rose, by reason of the heat driving off occluded or adherent gases from the glass and metal surfaces, to about  $\frac{1}{80}$  mm. Long-continued heating with this single bunsen-burner did not noticeably reduce the P.D. between the metals, so an additional source of heat was applied in the shape of another burner; but after a couple of hours' heating and pumping, although air still continued to come off, no change in the P.D. was observed after the metals were allowed to cool.

The tube was next heated in a blowpipe flame, the outer copper shield being kept at a red heat for about 10 minutes. Copious air-bubbles now passed through the fall tubes of the sprengel-pump, and the pressure fell from  $\frac{1}{2000}$  millim. to  $\frac{1}{100}$  millim. The apparatus was then allowed to cool, the pump being worked continuously. When it was quite cold the pressure was  $\frac{1}{6000}$  millim., and the P.D. had fallen to about 0·1 of a volt. It will be seen from § 10 that this was simply the result of oxidation of the zinc, but at the time I thought it might have possibly been a true diminution of the Volta effect due to my having driven off the greater part of the condensed air from the surface of the metal plates. I therefore again heated the tube in the blowpipe flame, this time more strongly than before. Unfortunately the heat

proved too fierce for the zinc plate, for it volatilized, covering nearly the whole of the inside of the apparatus with a fine layer of zinc dust. The tube therefore had to be dismantled and opened, thoroughly cleaned, and a fresh plate of zinc put in place of the old one. I thought it best this time not to use the blowpipe at all, but merely to heat the apparatus with a couple of bunsen-burners, continuing heating and pumping until no more air should come away through the pump. But here again, after about five hours' heating, the zinc again melted and the experiment proved useless. I then decided to dispense with the zinc plate altogether and to replace it by a plate of aluminium, whose melting-point is  $600^{\circ}$  C., while that of zinc is  $412^{\circ}$  C.

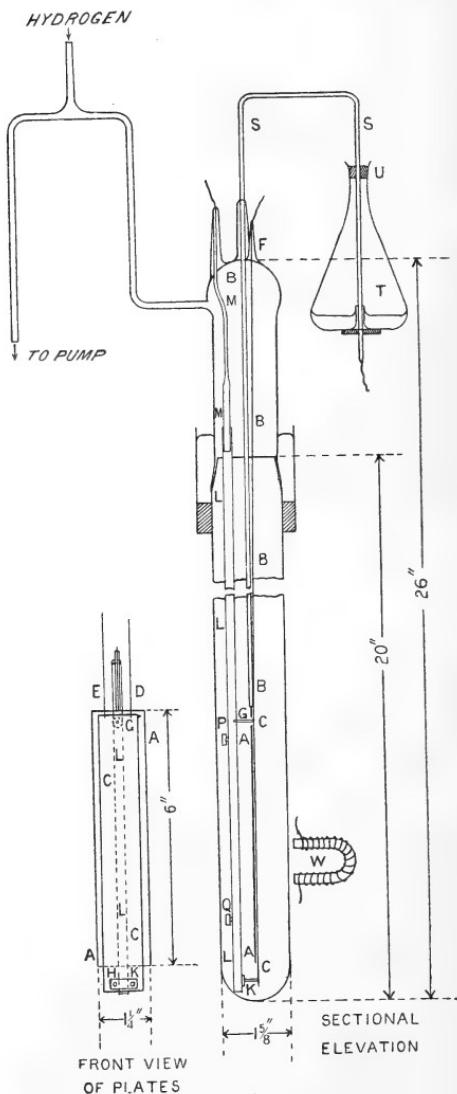
In the course of the next series of experiments I unluckily broke both the upper and lower parts of the tube just at the middle joint C, C in exercising a little too much vigour in separating the two parts from one another after the usual persuasive means of loosening obdurate ground-glass joints had proved unsuccessful. As the apparatus had to be entirely remade I introduced some radical changes in its construction in order to remedy the inherent defects of the original design.

§ 9. Fig. 3 represents the new apparatus as finally constructed. I here adopted the original Volta method of procedure, with the application, of course, of Lord Kelvin's compensation device. In this particular form of apparatus, where great capacity can only be attained by diminishing the distance between the condenser-plates, it is susceptible of greater sensibility than the Ayrton and Perry modification, and it is, moreover, somewhat simpler.

In the fig. A, A is the insulated platinum plate supported and insulated by the glass tube B. To insure rigidity, the plate was fairly stout, too thick to be fused into the glass support, so that it had welded to the top a stout piece of platinum wire which fitted tight into the glass tube B. C, C forms the second plate of the contact couple (at first aluminium and afterwards iron). It is suspended by two very fine platinum wires D and E (front view of plates) that are sealed into the upper part of the apparatus F, so that when C hangs freely, it does so parallel and very close to A, A. The plates are prevented from coming into contact by the three stops G, H, and K. The stop G screws into the aluminium tube L; H and K into the small cross-piece that is shown in the figure (side view of plates). The tube L fits tightly over the glass rod M that is fused into the head of the tube. A platinum wire which runs down M serves to earth the tube L. The latter tube also serves another purpose, namely, to carry on the small aluminium supports P and Q an electro-

static shield of aluminium that half encompasses the insulated plate A, A. (It is not shown in the figure.) The shield has two

Fig. 3.



slits shaped thus  that just slip over the heads of P and Q. It was not necessary to completely shield A, A, as the plate C, C itself, which is of course earthed, serves as a partial

shield. In other respects the apparatus is essentially the same as the older one which it replaced.

There is no need to discuss here the well-known method of making an observation. In the actual apparatus (fig. 3), C, when not of iron, had a plate of that metal attached to its back, so that by closing the circuit of the small electromagnet W by means of a spring key it was drawn away from the platinum plate A. This reduced the taking of a reading to the exceedingly simple operations of making and then breaking a single platinum contact to the potentiometer, and then pressing a spring key.

In its new form the apparatus proved entirely satisfactory in every way. The adjustments were not at all troublesome to make, in fact, it was eventually found possible to dispense altogether with the stops L, H, and K (fig. 3), for the plates could be prevented from touching and yet allowed to come within  $\frac{1}{15}$  in. of one another by just giving the proper tilt to the apparatus as a whole. The sensibility was all that was desired. When that of the quadrant electrometer for directly applied E.M.F.s. was 553 scale-divisions per volt, a P.D. between the condenser-plates of 1 volt gave on the average a deflexion of about 70 on pulling away the movable plate. It was quite possible, by taking great care in making the adjustments, to attain a sensibility of 90 divisions per volt. The readings in general are accurate to 0·02 of a volt, and they are pretty reliable to 0·01 volt.

§ 10. The experiments were continued with this improved apparatus, using plates of aluminium and platinum as the dissimilar metals. The P.D. between these metals measured as quickly as possible after cleaning the surface of the aluminium with fine emery-paper was

$$1\cdot45 \text{ volts.}$$

This value slowly fell as time went on\*; thus after about  $1\frac{1}{2}$  hours, it was

$$1\cdot20 \text{ volts;}$$

and it finally assumed, very slowly, a steady value of about

$$1\cdot02 \text{ volts.}$$

After this steady value had been arrived at, the experiment was proceeded with much as described in § 8. The tube was exhausted to about  $\frac{1}{200}$  millim. pressure, and then heat was applied from two bunsen flames. The variations of pressure

\* Erskine-Murray on "Contact Electricity of Metals," Proc. Roy. Soc. vol. lxiii. p. 124.

that followed were similar to those observed in the old apparatus (§ 8). Even after heating in this way for five hours the pressure was about the same as at the beginning of the operation (it varied from  $\frac{1}{170}$  millim. to  $\frac{1}{230}$  millim.), showing that after prolonged heating condensed air was still given off from the inside surfaces of the apparatus. This did not, of course, necessarily imply that there was still a large quantity of air left sticking to the metal plates, for as the heat slowly travelled up the tube by conduction air would be gradually driven off its upper surfaces, and this would continue until the whole of the apparatus (and even the pump) became strongly heated. The source of heat was very gradually removed, the pump being vigorously worked the whole time, until when the tube was quite cold the pressure was  $\frac{1}{2500}$  millim. The P.D. between the plates was then

0·28 volt.

(I could never get a satisfactory reading until the tube was quite cold, for on insulating the platinum plate and its connected quadrants there was always a considerable leakage of electricity into the plate, possibly by convection from the surrounding gaseous molecules.)

After leaving the apparatus for 15 hours the pressure had risen to  $\frac{1}{80}$  millim., and then the P.D. was

0·31 volt.

On exhausting to  $\frac{1}{8000}$  millim. (without further heating) the P.D. was still

0·31 volt.

Air was then admitted into the tube. The reading remained unaltered even after several hours, but after leaving the tube open to the atmosphere for three days, the P.D. had fallen to

0·02 volt.

The aluminium plate was then taken out and very gently rubbed once or twice with fine emery-paper. The P.D. rose to

0·56 volt.

It was again rubbed with emery, after which the P.D. was

0·72 volt.

It is thus clear that at least the greater part of the above diminution of the contact effect was due to some change of surface of the aluminium plate, most probably oxidation, since it was a permanent effect and only removed by cleaning the plate, and also because almost the same phenomenon took

place when the tube was heated under exactly the same conditions but in this case full of air, for on doing so the P.D. fell to

0·30 volt

when cold, and rose again to

1·10 volts

on thoroughly cleaning the aluminium.

§ 11. The experiments described in § 10 satisfied me that it was useless to attempt to drive off the last remnants of air from the metal plates by merely heating them in a vacuum, so I decided first to thoroughly wash out the apparatus three or four times with fairly pure dry hydrogen, and then strongly heat it in a high vacuum of that gas. I expected that such a molecularly active gas as hydrogen would displace even the last traces of air from the pores of the metal plates.

The hydrogen was prepared from fairly pure zinc (such as is used in Marsh's test for arsenic) and pure hydrochloric acid. It was washed by passing through distilled water and carefully dried by means of tubes of pumice and strong sulphuric acid and of phosphorus pentoxide. Such hydrogen should contain but the barest traces of foreign gases, and I considered it sufficiently pure for my purpose. (I had tried other methods of preparing the hydrogen, but found the above the most satisfactory on the whole. The chief thing was to avoid having such impurities in the gas as oxygen, ozone, water-vapour, or other oxygen-containing electrolytes.) There was probably a far greater quantity of strange gases in the vacuum-tube even after exhaustion than was in the hydrogen.

The hydrogen generating apparatus and drying-tubes were joined directly to the apparatus through a mercury-sealed tap. The generating apparatus, when not producing gas, was always kept full of hydrogen at a pressure greater than that of the atmosphere, so that if any leakage took place through the various joints it would be hydrogen leaking out into the atmosphere and not air leaking in.

§ 12. At the beginning of this new experiment the P.D. between the plates was

0·98 volt.

I exhausted to a vacuum of  $\frac{1}{3000}$  mm., and let in hydrogen until the pressure was 1 atmosphere. The P.D. fell to

0·91 volt.

I then again exhausted to a pressure of  $\frac{1}{200}$  mm., when the P.D. was

0·95 volt,

and again let in an atmosphere of hydrogen. The same operation was repeated a third time, and finally the apparatus was left to itself full of hydrogen for two days, so as to give the gas a good chance of soaking into the metals and displacing from them the original surface-layers of air. The voltage was then

0·87 volt,

and remained constant at that value. (This diminution is in accordance with Lord Kelvin's observation that soaking a platinum plate in hydrogen makes it temporarily about 0·1 volt positive to another platinum plate that has not been so treated\*.)

I then again exhausted to  $\frac{1}{5000}$  mm. and heated the tube with a couple of bunsen-burners just as on former occasions. When cold the P.D. was

0·83 volt,

at a pressure of  $\frac{1}{10,000}$  mm.

From the practical constancy of this value, it seemed to me that I had now really removed the last traces of air, and that there was not sufficient oxygen present to oxidize the aluminium plate as had happened before in an ordinary vacuum, and that there was a true contact P.D. between aluminium and platinum of about 0·8 of a volt. To subject it to the severest possible test, I next heated the apparatus to a far higher temperature with a blowpipe-flame. The outer copper protecting sheath was kept red hot for about half an hour, the pump working throughout the time. I then allowed the tube to slowly cool. When it was quite cold and the pressure was  $\frac{1}{10,000}$  mm., the P.D. between the plates was

0·09 volt.

I let in a little hydrogen; it had no immediate effect on the P.D. I then let in dried air; the reading very slowly fell to zero, and the next morning it was

-0·15 volt

(*i. e.* aluminium negative to platinum), at which value it remained permanently. In appearance the aluminium was unaltered, except for a very slight purple coloration just at

\* 'Nature,' April 4, 1881.

the bottom of the surface facing the platinum. Cleaning it well with emery-paper sent back the value to

1·20 volts.

Thus we have arrived at the exceedingly interesting fact that even in a *high vacuum of pure dry hydrogen at the minute pressure of  $\frac{1}{10,000}$  mm. of mercury, and after four washings in that gas, there is still sufficient oxygen present to completely oxidize the surface of an aluminium plate*, if it only be brought to a sufficiently high temperature (about a dull red heat); and if there is sufficient oxygen present to oxidize it there is surely sufficient present to charge it as required by the electrolytic theory of the Volta effect.

In face of this striking experimental result, it is utterly futile to draw any positive conclusions whatsoever concerning the seat of the E.M.F. in Volta's phenomenon based on experiments made in what usually passes for a vacuum, whether it be a vacuum of air or one of any other gas; because, to repeat what I have already stated, unless far more drastic measures are taken—and no mere mechanical pumping will suffice—it is a matter of practical impossibility to remove the insoaked condensed air-films from the surfaces of such highly oxidizable metals as zinc and aluminium. And yet the most illustrious upholder of the contact theory asks concerning Dr. Bottomley's high-vacuum experiments (referred to above, § 1), made in a vacuum of  $\frac{1}{523}$  mm. and without any application of heat, what would be the efficacy of the supposed oxygen bath in such a case! \*

§ 13. In face of these results, a perfectly decisive experiment seemed almost hopeless to expect. However, I finally decided upon a method of removing the whole of the oxygen which really did offer some hopes of success, and that was to *chemically burn away the oxygen*. Such a process naturally could not be carried out with aluminium as the positive metal, simply because aluminium has a greater affinity for oxygen than has hydrogen, and it is impossible under any known circumstances to reduce aluminium oxide by means of hydrogen. Iron, however, was a metal that answered all the necessary requirements. The P.D. between it and platinum was sufficiently high (it varies from about 0·3 to 0·5 of a volt, according to surface conditions) for the purpose; the metal could be very strongly heated without fear of fusion or volatilization, and any oxide of iron present or formed in the process of heating could be easily reduced by

\* Phil. Mag. vol. xlvi, p. 82 (1898).

hydrogen at a not unduly high temperature. There is another property possessed by iron which is of peculiar interest in connexion with these experiments, namely, its transparency to hydrogen at a red heat\*. Owing to this remarkable and interesting property (which is likewise shared by platinum), it seemed probable in the highest degree that after the continued heating of such a platinum-iron couple in an atmosphere of hydrogen, the gas would freely permeate both metals and eventually combine with every trace of oxygen present, either directly or by reducing any iron oxide that has been formed, and the product of the combustion (water) would be driven off by the heat and absorbed in drying-tubes of phosphorus pentoxide. Of course I did not expect that all the oxygen would be removed in one operation; but that if the metals were brought to a red heat and then allowed to cool (both iron and platinum absorb hydrogen on cooling) and the operation repeated say half-a-dozen times, that little by little the whole or at least the greater part of the oxygen films condensed on the surface-layers of the metals would be driven off and replaced by hydrogen. Thus it would be possible to measure the contact P.D. between iron and platinum in an atmosphere of hydrogen and of *hydrogen only*. As has already been pointed out, it is useless to displace the outer atmosphere of hydrogen and to leave the inner layers of gas whose particles are within the range of molecular action of the metals unchanged (see § 1). From what follows (§ 14), I venture to think that as far as my experiments go they seem to confirm on the whole and within certain limits the series of phenomena that were suggested above as being likely to take place.

§ 14. The iron used was a piece of commercial sheet-iron. I should have preferred to use pure iron, but it would have had to be specially rolled, and as I was greatly pressed for time that operation would have taken longer than I could afford to wait.

In order to work with as large a P.D. as I could possibly get, I thoroughly cleaned and burnished the surface of the iron †; the P.D. between the burnished iron and platinum was

0·50 volt.

The next day it had fallen to

0·37 volt

\* Discovered by Graham: see his 'Collected Papers,' p. 279.

† See Dr. J. Erskine-Murray, "On Contact Electricity of Metals," Proc. Roy. Soc. vol. lxiii, pp. 117-122.

(Dr. Erskine-Murray does not mention that the high potential produced by burnishing is merely a temporary effect), and remained practically constant at that value. I then exhausted and washed out the apparatus with hydrogen and repeated the process three times just as described in § 12. The tube was then heated with a blowpipe-flame and kept at a bright red heat for about 20 minutes. It was then, of course, full of hydrogen, at about an atmosphere pressure (when hot). Knowing the pressure of the gas in the tube both when it was hot and cold I was able, by making certain assumptions as to the distribution of heat, to roughly estimate the maximum temperature of the gas in the tube. After keeping the outside copper tube at a bright red heat for about 40 minutes the maximum inside temperature was not less than 800° C.

The next morning the P.D. was

—0·40 volt (platinum positive to iron).

I then heated again, as before, for 33 minutes ; when cold, after about three hours, the P.D. was

—0·06 volt.

I again heated for half an hour. The next morning the reading was

—0·28 volt.

I heated again for half an hour. After three hours the P.D. was

—0·05 volt.

I repeated the operation. The next day the P.D. was

—0·13 volt.

On again heating for half an hour the P.D., as measured after two hours' cooling, was

+0·05 volt.

I further heated for 35 minutes. In two hours and a half the P.D. was

—0·02 volt.

I heated again for half an hour. The next morning the voltage stood at

—0·16 volt.

I had hoped that after so many successive heatings and coolings the P.D. would have settled down to a steady value after all the oxygen had been got rid of, and that this value would be the true contact P.D. in an atmosphere of hydrogen. But,

as is evident from the above readings, such was not the case; there seemed to be no tendency for the voltage to settle down to a final steady value. However, a careful examination of the above results and of others not given here, convinced me that there is a law underlying these results in spite of their apparently contradictory nature. It seems that, on the whole, readings that were taken as soon as possible after the heating (the tube, however, being cold or almost cold) were more positive (or less negative) than those taken some hours or on the next day after the heating. In order to test this supposition, when I next repeated the operation of heating, I took time-readings of the voltage, starting as soon as possible after the heating. There is really a double time effect taking place, the one superimposed upon the other: firstly, an ordinary temperature effect; this ceases when the tube is quite cold or soon after; secondly, the time effect particularly referred to here, which goes on, as will be seen, for several days, long after direct temperature effects have disappeared. In consequence of this the time-readings taken, say within the first two or three hours after heating, teach us nothing definite.

The tube was kept red hot for half an hour from 2.20 to 2.50 P.M., and then the asbestos-lined copper shield was immediately removed so as to allow it to cool as quickly as possible. At 3.30, when the apparatus felt almost cold, the P.D. was

	0.18 volt.
At 3.50 it was	0.04 volt.
At 4.25 it was	-0.12 volt.
At 5	-0.15 volt.
At 8	-0.20 volt.

The next day at 10.30 A.M., -0.29 volt.

After two more days, at 10.30, -0.60 volt.

The temperature-E.M.F. curve becomes asymptotic at about -0.60 volt.

On repeating the operation by again heating and taking time-readings, I obtained very similar results. In this case the P.D. after twenty-three hours was

-0.28 volt,

and I then started exhausting the apparatus of hydrogen (although the equilibrium value, -0.60 volt, was not yet arrived at) with the intention of again letting air into the

tube. When the pressure was  $\frac{1}{330}$  mm. the P.D. was  
 $-0\cdot33$  volt.

I then again let in a little hydrogen, 1 mm. merely ; the P.D. immediately became relatively more positive, it being

$-0\cdot54$  volt. (*Cp. § 12 above.*)

On again exhausting, the P.D. fell ; when the pressure was  $\frac{1}{100}$  mm. the reading was

$-0\cdot42$  volt,

and at  $\frac{1}{300}$  mm.

$-0\cdot35$  volt,

just as before, at about the same pressure. I again let in a little hydrogen, this time 3 mm. ; the P.D. became

$-0\cdot48$  volt.

I then let in dry air, until the pressure was 1 atmosphere. The P.D. then moved slowly in the positive direction. The air was admitted at 6.35 P.M.

At 6.47 the P.D. was  $-0\cdot43$  volt.

At 7.0 it was  $-0\cdot40$  volt.

At 7.20  $-0\cdot37$  volt.

The next morning at 10.30 it was

$-0\cdot17$  volt.

This very slow return to the positive value, or, rather, in the positive direction, is just what one would have expected on the assumption that the Volta effect is a function of the medium surrounding the gases. Consider for a moment the state of the surfaces of the metals just at this juncture. The whole object of the experiment was to remove, to the utmost extent possible, the original condensed surface-layers of air from the plates, and to replace them by layers of hydrogen. From the method that was adopted, and from the results that followed, it is almost certain that this state was actually arrived at. Then the true contact P.D. between iron and platinum in an atmosphere of hydrogen *and hydrogen only* (neglecting for the moment the probably inactive nitrogen) is about  $-0\cdot60$  volt (platinum being positive to iron). The fact that this value was only reached long after the metals had cooled from a red heat in an atmosphere of hydrogen is easily explicable. The whole or greater part of the Volta effect is due to the layers of gas in immediate and close contact with the metal surfaces. Naturally, when the metals were hot,

the amount of gas (in this case hydrogen) in such close contact was extremely small. As the metals cooled—and, indeed, long after they were cold—they were gradually soaking in and absorbing hydrogen ; and all the time this was going on the P.D. was gradually becoming more and more negative (see p. 86), until at last the final value, about  $-0\cdot60$  volt, was reached, and this represents *the true value of the Volta effect between iron and platinum in an atmosphere of hydrogen*. When, then, I pumped out the hydrogen and let in air, the P.D. did not immediately return to its original positive value, although it slowly went back in the positive direction (no more than measuring the contact P.D. of air-covered plates of iron and platinum in hydrogen gives a P.D. of  $-0\cdot60$  volt) simply because the greater part of the gas in the closest contact with the metals was still hydrogen and not air. The metals would probably have to be left for months, and perhaps years, before the air would entirely replace the surface-layers of hydrogen. In fact, it would possibly be as difficult to replace the hydrogen film by an air film as it was to displace the original air film and replace it by hydrogen. Nevertheless, the all-important fact remains that a complete change of atmosphere, unaccompanied, as far as the chemical conditions enable us to judge, by any corrosion or oxidation of the metallic surfaces, induces a complete and fundamental change in the value of the Volta effect, differing not only in magnitude but also in sign from the first value. It would be well, if this experiment be repeated, to actually leave the metallic couple untouched for some considerable time (some weeks or even months if necessary) to see whether the maximum positive value of the P.D. would return of its own accord without external aid. In this case I thought I might hasten somewhat the process of replacing the new hydrogen-film again by an air-film by heating the tube. I kept the outside copper sheath red hot for about 15 minutes. When the tube was perfectly cold the P.D. was

$$+0\cdot22 \text{ volt.}$$

After two hours it remained entirely unaltered at  $0\cdot22$  volt. It might be objected that heating in this way oxidized the iron ; but it must be remembered that the plates were still partially surrounded with hydrogen, and before oxidation could take place the hydrogen would have to be driven off. (In any case, at a red heat any oxygen present would unite with the hydrogen rather than with the iron.) This view is supported by the result of a second heating, in this case extending over 20 minutes. Then, after the tube was cold,

the P.D. was exactly zero, and on taking out the iron plate and examining it I found it completely covered with a thin black scale of iron oxide. There is no doubt, then, as to the effect of surface oxidation ; and it is in agreement with other experimenters, who find that oxidation always causes the contact activity of metals to disappear.

§ 15. The net result of the experiments described above in § 14 is strongly in favour of that theory of the Volta effect which supposes it to be due to some electrolytic action of the medium or media surrounding the dissimilar metals \*. We have seen how, by as far as possible removing the oxygen from the surfaces of an iron-platinum couple and replacing it by hydrogen, there resulted an enormous total change in the contact E.M.F., namely from +0·37 volt to -0·60 volt; how on again admitting air, so that a mixture of air and hydrogen surrounded the plates, the P.D. slowly moved in the positive direction, reaching after 16 hours a value of -0·17 volt ; and how, after heating the plates so as to artificially hasten the removal of hydrogen from the surfaces of the metals and its replacement by air, the value of the P.D. became still more positive, namely +0·22 volt. There is a strong presumption of truth in the assertion that these curious variations in the contact force under varying conditions of atmosphere, which become so intelligible when looked at in the light of the electrolytic theory, appear impossible and incomprehensible when considered from a standpoint like that taken up by the pure contact theorists.

§ 16. This investigation does not in any way pretend to be final: it is hardly more than preliminary; but I venture to think that I have accomplished, or at least got near accomplishing, what has never before been attained in the history of contact electricity; namely, the entire removal (by chemical means) of the "ancient air-sheets" from the surfaces of the metals and making measurements in an entirely different medium, without at the same time permanently altering the surfaces of the metals by causing them to form salts (as happened, for instance, in the valuable experiments of Mr. J. Brown †). Unfortunately, circumstances compelled me to abandon this work for the time being, and thus prevented me from continuing experimental investigations in the same direction.

\* The supposed mechanism of this action I need not discuss here. Valuable and ingenious suggestions on this head have been made by Prof. Oliver Lodge in his Report to the British Association in 1884, quoted above, and they have been further elaborated in an interesting series of letters that passed between Prof. Lodge and Prof. Burnside in the columns of 'Nature,' vol. xliii.

† Phil. Mag. Aug. 1878, and Feb. 1879.

But there are one or two experiments that might be suggested that could be very easily performed without any special expensive or complicated apparatus. Thus it would be very interesting to keep an iron plate red hot in a stream of pure dry hydrogen for several hours, allow it to cool in that gas, leaving it say for a few days, and then measure the contact P.D. between it and another iron plate that had not been so treated. This might be repeated with a platinum plate, and the two experiments together would then be somewhat equivalent to those described on pp. 85-87, and very much simpler to perform.

§ 17. It is with the hope that somebody will find it worth while to continue investigations along these lines, that I venture to publish these preliminary results\*.

Throughout the whole of this work I have been fortunate enough to receive the valued assistance and advice of Prof. W. E. Ayrton, F.R.S., in whose laboratories at the Central Technical College the work was done, and of Mr. T. Mather, his Senior Demonstrator in the Physical Department. I must also thank my friend Mr. W. Duddell and Mr. W. T. Evans, who have so often kindly helped me, when necessary, in the experimental part of the work.

*V. On the Expansion of Porcelain with Rise of Temperature.*  
By T. G. BEDFORD, B.A., Sidney Sussex College, Cambridge†.

**I**N experiments involving the use of air-thermometers, such as comparisons between the air and platinum-resistance scales of temperature, a correction is required for the expansion of the thermometric envelope. Over a range at low temperatures the expansion might be readily determined, *e. g.*, by filling the bulb with a liquid, conveniently mercury, whose absolute expansion is known, and using it as a weight-thermometer to measure the relative expansion of the liquid. At high temperatures, however, such a method cannot well be used, and the correction must be calculated either from the results of low temperature measurements, or from the linear expansion as determined directly at these higher temperatures, provided the material be homogeneous. As porcelain is the substance generally used, this latter method is available; and it was therefore suggested to me by Mr. E. H. Griffiths, F.R.S., that it might be useful to try

\* Since the above was written I am very pleased to be able to add that Mr. H. Tomlinson has now taken up the thread of this research, working, for the present, with my old apparatus, and starting from the point at which I left off.

† Communicated by the Physical Society.

to determine how the expansion of porcelain varies with the temperature.

Direct determinations of the linear expansion of porcelain have been made by Deville and Troost (*Comptes Rendus*, lix. p. 162, 1864), and by Holborn and Wien (*Ann. Phys. Chem.* xlvi. p. 107, 1892). In the experiments of Deville and Troost on Bayeux porcelain the temperatures were measured by means of an air-thermometer heated in the same enclosure with the experimental rod, and having its bulb of the same kind of porcelain. Readings were taken at 0° C. and again at temperatures between 1000° and 1500°. The conclusion reached was that the coefficient of cubical expansion is constant, and between .000016 and .000017. In the experiments of Holborn and Wien the expansion of a length of 9 cm. of Berlin porcelain was measured, the temperature being determined by a thermo-electric junction in contact with the porcelain. Measurements were taken at the temperature of the room, and again at about 1000° in some experiments, at about 500° in others. As the values found for the mean coefficient for one of these intervals agreed as well with those found for the other interval as they did amongst themselves, these experimenters also concluded that the coefficient is constant. The mean value of the coefficient of linear expansion for the kind of porcelain used for their air-thermometers is taken as .0000044.

The method adopted in the experiments described in the present paper was essentially the same as that employed in the case of *glass* by Callendar (Phil. Trans. 1887 A, p. 167), and by Callendar and Griffiths (Phil. Trans. 1891 A, p. 123).

A tube of glazed Bayeux porcelain about 1 metre long and 1.7 cm. external diameter was used. Two fine transverse scratches ran round the tube at a distance of about 91 cm. from each other ; and the distance between these marks was directly compared at a series of temperatures from 0° C. to 830° C. with a standard length, by means of a pair of reading microscopes.

The mean temperature of the portion of the tube between the marks was deduced from the resistance of a platinum wire (doubled for the sake of obtaining a convenient value for  $R_{100} - R_0$ ) which passed straight down the tube from one mark to the other and back again. The wire was fastened down at intervals to a strip of mica which fitted the tube fairly tightly. At the upper mark the wires were attached to others of thicker platinum, which were themselves joined at the pyrometer-head which closed this end of the tube to

copper leads. The head also carried a second pair of terminals to which was attached a thick platinum wire running to the upper mark and back to act as a "compensator."

Connexion was made between the pyrometer-head and the resistance-box by means of a carefully equalized and insulated fourfold cable. The lower end of the porcelain tube was closed by a porcelain plug.

The resistance measurements were made by the usual Wheatstone-bridge method, the arms of the bridge being equal. The resistance-box used contains a set of 7 coils of nominal values 10 to 640 mean box-units, and in series with the coils a bridge-wire 40 cm. long, the effective resistance of 1 cm. of which is equal approximately to 1 box-unit. By means of a vernier .01 cm. can be read. The mean box-unit is roughly .01 ohm \*. A careful standardization of both coils and bridge-wire was made in January 1898, by Mr. E. H. Griffiths and Mr. C. F. Green; and again in May 1899, since the completion of these experiments, the coils have been restandardized by Mr. C. F. Green, and show no perceptible change since the previous standardization. The resistance of the pyrometer-wire was about 260 box-units at 0° C. The current from a dry cell through 20 ohms was employed, and was found to produce no serious heating-effect. Thermo-electric effects were eliminated by the use of Griffiths' Thermo-electric key (*Phil. Trans.* 1893 A, p. 398). A dead-beat mirror galvanometer was used.

The reading-microscopes, for the use of which the writer is indebted to Prof. Ewing, were made by the Cambridge Scientific Instrument Company. They were supported on solid stone blocks standing on a firm stone bench. The microscope-carriage moves along its slides by means of a screw of .5 mm. pitch, the head being divided into 100 parts and thus reading to .005 mm. Tents of these divisions could be estimated, but the diamond marks on the porcelain were not sufficiently good to enable settings of the cross-wire to be made to such accuracy. The gas furnace in which the tube was heated was supported on a stand provided with levelling screws, by adjusting which the marks were kept in focus as the tube was heated or cooled. Both the microscopes and bench were screened by bright tinned plate from the radiation from the furnace. As a standard length the distance between two diamond marks on a glass tube kept in a trough of melting ice was used. This distance was equal to 91.394 cm. During each experiment the readings for the glass tube were taken at intervals.

\* There is a full description of a box of this type, known as the "Student's Box," in the 'Electrical Review,' Aug. 18, 1899.

For the determination of the fixed points  $R_0$  and  $R_{100}$ , the apparatus was more cumbersome than that used for smaller pyrometers. In determining  $R_{100}$ , steam from a boiler was led into a metal tube about 6 cm. in diameter surrounding the porcelain tube. The metal tube was surrounded by a similar wider tube 10 cm. in diameter and co-axial with it. The steam, passing along the inner metal tube, returned through the space between the two tubes, forming a jacket, and thence passed out to a condenser. A siphon-gauge showed any excess of steam-pressure within the apparatus above the atmospheric pressure. The jacketed steam vessel and the tubes leading from the boiler were carefully packed round with cotton-wool and hair felt. The steam-vessel was slightly inclined to the horizontal, so that the condensed water might drain away. It was found that with this arrangement the readings very soon became steady when steam was passed into the apparatus; and the values of  $R_{100}$  deduced from experiments on different days and under different barometric pressures agreed satisfactorily with one another.

The ice-point  $R_0$  was determined by immersing the porcelain tube in a mixture of pounded ice and water contained in a vessel formed from the larger of the metal tubes used for the steam-point determinations.

The sample of platinum wire, from which the piece used in these experiments was cut, is known to have a value of  $\delta$ , in Callendar's formula, from 1.50 to 1.51. The value  $\delta=1.505$  was assumed, and thus a direct determination of the resistance at the temperature of boiling sulphur was avoided. An error of .01 in  $\delta$  causes an error of less than  $1^\circ$  in the calculated value of  $t$  at  $1000^\circ$ .

After a careful determination of the ice and steam points, the tube was heated as follows :—

TABLE I.

Number of Expt.	Date.	Maximum Temperature.	Number of Expt.	Date.	Maximum Temperature.
1.....	March 13.	77° C.	6.....	March 29.	810° C.
2.....	, 17.	319	7.....	, 30.	824
3.....	, 21.	650	8.....	April 3.	828
4.....	, 23.	640	9.....	, 7.	821
5.....	, 24.	740	10.....	, 8.	840

After the experiment of March 30, the ice and steam points were re-determined, and were found to have changed considerably. Accordingly, from this date, a re-determination of the fixed points was made after each exposure to a high temperature, and the values then obtained were used in the reduction of the observations of the preceding experiment. On account of the change, the observations of March 21-29 inclusive were not reduced.

In making an experiment the tube was heated to as high a temperature as possible, and observations of length and resistance were made. By diminishing the gas-supply the tube was then allowed to cool gradually, and when the temperature had become steady, length and resistance measurements were again made; this process was repeated till the tube reached the temperature of the air. The observations were recorded thus:—

TABLE II.

Time.	Glass tube.	Bench.	Porcelain tube.	R. L.	Coils.	Bridge wire.	Temp. of Coils.
7.37 P.M.		14.65	10.1285	70, 50	D, H	+1.5	15.63
7.54 ,,	10.4212	14.65					
8.17 ,,		14.9	10.2045	60, 40	B, C, E, F, G	+3.6	14.9

Columns 2 and 4 give the sum of the microscope readings for the standard length and the porcelain tube respectively. The porcelain tube projected from the furnace so that a length of about 6 cm. at either end was not directly heated thereby. The temperature of the tube in the neighbourhood of the marks was taken roughly by means of mercury thermometers, and is recorded in column 5.

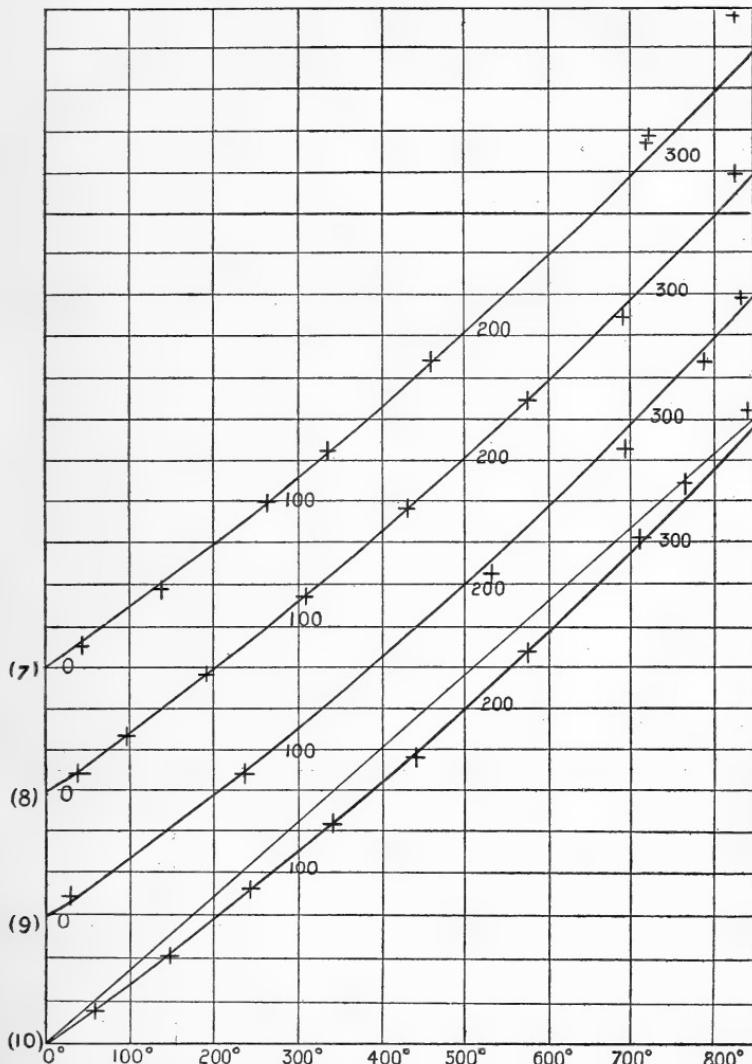
The results of experiments 1, 2, 7-10, are collected in Table III. (p. 96); the results of the last four experiments are represented in the diagram.

It appears from the diagram that, from  $0^\circ$  to  $600^\circ$ , the results are represented fairly well by a curve given by the formula

$$l_t = l_0(1 + 34.25 \times 10^{-7}t + 10.7 \times 10^{-10}t^2).$$

Above  $600^\circ$  the points are more erratic, but at these higher temperatures the length measurements were somewhat difficult to make; moreover, as no gas-regulator was available,

it was impossible to keep the temperature quite steady during an observation. For comparison with the experimental numbers given in column 6, which represents the expansions reduced to unit length at  $0^{\circ}\text{ C}$ . column 7 gives



Ordinates : expansion per unit length : unit  $10^{-5}$ .  
 Abscissæ : temperatures centigrade.

(The straight line above the lower curve represents the expansion according to Holborn and Wien's coefficient.)

the corresponding values calculated from the formula; the full curves in the diagram are also drawn from the formula. The straight line in the diagram represents the expansion as given by Holborn and Wien's coefficient.

TABLE III.

No.	Date.	R.	t.	Lengths in cm.	Expansion per unit length.	From formula.	
1.	Mar. 13	277·5 341·0	14·1 77·4	91·3728 ·3910	$6 \times 10^{-5}$ 26	$5 \times 10^{-5}$ 27	$l_0$ 91·3673 (1) $R_0$ 263·073
2.	Mar. 17	274·7 572·3	11·4 318·8	·3716 ·4781	4 120	4 120	$R_{100}$ 363·358 $l_0$ 91·3683 (2)
7.	Mar. 30	1004·6 925·9 924·2 703·6 589·3 520·7 388·0 303·5	824·2 724·9 723·4 462·4 336·5 263·0 136·4 42·0	·7421 ·6744 ·6716 ·5519 ·5006 ·4733 ·4272 ·3957	392·5 318·5 315·5 184·5 128·5 98·5 48 13·5	355 304·5 303·5 181 127·5 97·5 48·5 14·5	$l_0$ 91·3833 $R_0$ 260·467 $R_{100}$ 361·788
8.	(Apr. 3 Apr. 3)	277·0 1005·4 898·2 801·4 675·1 561·7 454·3 360·7 299·0	16·1 827·5 692·5 576·3 431·5 307·3 194·2 98·8 37·3	·3860 ·7165 ·6381 ·5912 ·5318 ·4834 ·4413 ·4084 ·3877	3 372 286 235 170 117 71 35 12	5·5) 357 288·5 233 167·5 115 70·5 35 13	$l_0$ 91·3765 $R_0$ 260·875 $R_{100}$ 361·903
9.	Apr. 7	996·4 971·3 897·1 762·8 495·3 291·2	821·5 789·2 695·6 534·3 237·7 29·0	·7036 ·6811 ·6336 ·5646 ·4552 ·3874	358 333·5 281·5 206 86 12	354 336·5 290 213·5 87·5 10	$l_0$ 91·3765 $R_0$ 261·8 $R_{100}$ 362·115
10.	Apr. 8	1011·4 957·4 920·2 801·9 681·8 593·4 502·6 406·6 315·6	839·5 770·0 723·1 579·3 440·9 342·5 245·0 145·1 53·1	·7316 ·6913 ·6633 ·6002 ·5404 ·5030 ·4678 ·4321 ·4023	379·5 335·5 304·5 235·5 170·5 129·5 91 52 19	363 327 303·5 234·5 172 130 90·5 52 18·5	$l_0$ 91·3848 $R_0$ 261·847 $R_{100}$ 362·306

The coefficient of linear expansion at  $t^{\circ}$  C. is given by

$$\frac{1}{l_0} \frac{dl}{dt} = 34.25 \times 10^{-7} + 21.4 \times 10^{-10}t.$$

Since the coefficient varies with the temperature, an uncertainty is introduced due to the gradient of temperature from the portion of the tube heated in the furnace to the marks ; but this uncertainty must be very small. According to a rough estimate made by the aid of the auxiliary temperature readings in column 5, Table II., the correction for the ends came out to be .6 per cent. at mean temperature  $800^{\circ}$ , falling to .4 per cent. at  $600^{\circ}$ .

The error introduced into the temperature measurements, if the part of the tube occupied by the wire did not precisely coincide with the part between the diamond marks, must also have been very small. Thus, for a temperature gradient so steep as  $100^{\circ}$  per centim. in the neighbourhood of the diamond marks, an error of  $1^{\circ}$  in the temperature would necessitate a displacement of the wire by nearly 1 centim. The chief difficulty in experiments of this kind seems to be in insuring that the temperature shall be uniform all along the tube. With an ordinary gas-furnace it is impossible to be certain that this condition is satisfied. An accident to the tube after experiment 10 prevented any further measurements, and so no experiments were made while the temperature was rising.

As may be seen from Table III., there seem to have been permanent changes in the length of the tube during the course of the experiments, but these changes are very small and apparently irregular. At the end of experiment 7 it was observed that the tube had become very slightly bent ; the irregularities in the length at  $0^{\circ}$  may be due to this. The total increase in length at  $0^{\circ}$  from March 13 to April 8 was .02 per cent.

For cubical expansions we get

$$v_t = v_0(1 + 102.75 \times 10^{-7}t + 32.4 \times 10^{-10}t^2);$$

and for the coefficient at  $t_0$ ,

$$\frac{1}{v_0} \frac{dv}{dt} = 102.75 \times 10^{-7} + 64.8 \times 10^{-10}t.$$

In conclusion the writer must express his indebtedness for the use of the Sidney College Chemical Laboratory, and also for help which he has received from Mr. C. F. Green, B.A., from time to time.

VI. *The Law of Partition of Kinetic Energy.*  
*By Lord RAYLEIGH, F.R.S.\**

THE law of equal partition, enunciated first by Waterston for the case of point molecules of varying mass, and the associated Boltzmann-Maxwell doctrine respecting steady distributions have been the subject of much difference of opinion. Indeed, it would hardly be too much to say that no two writers are fully agreed. The discussion has turned mainly upon Maxwell's paper of 1879†, to which objections ‡ have been taken by Lord Kelvin and Prof. Bryan, and in a minor degree by Prof. Boltzmann and myself. Lord Kelvin's objections are the most fundamental. He writes § : "But, conceding Maxwell's fundamental assumption, I do not see in the mathematical workings of his paper any proof of his conclusion 'that the average kinetic energy corresponding to any one of the variables is the same for every one of the variables of the system.' Indeed, as a general proposition its meaning is not explained, and it seems to me inexplicable. The reduction of the kinetic energy to a sum of squares leaves the several parts of the whole with no correspondence to any defined or definable set of independent variables."

In a short note || written soon afterwards I pointed out some considerations which appeared to me to justify Maxwell's argument, and I suggested the substitution of Hamilton's *principal* function for the one employed by Maxwell¶. The views that I then expressed still commend themselves to me; and I think that it may be worth while to develop them a little further, and to illustrate Maxwell's argument by applying it to a particular case where the simplicity of the circumstances and the familiarity of the notation may help to fix our ideas.

But in the mean time it may be well to consider Lord Kelvin's "Decisive Test-case disproving the Maxwell-Boltzmann Doctrine regarding Distribution of Kinetic Energy"\*\*\*, which appeared shortly after the publication of my note. The following is the substance of the argument :—

"Let the system consist of three bodies, A, B, C, all movable only in one straight line, K H L:

\* Communicated by the Author.

† 'Collected Scientific Papers,' vol. ii. p. 713.

‡ I am speaking here of objections to the dynamical and statistical reasoning of the paper. Difficulties in the way of reconciling the results with a kinetic theory of matter are another question.

§ Proc. Roy. Soc. vol. 1. p. 85 (1891).

|| Phil. Mag. Apr. 1892, p. 356.

¶ See also Dr. Watson's 'Kinetic Theory of Gases,' 2nd edit. 1893.

\*\* Phil. Mag. May 1892, p. 466.

"B being a simple vibrator controlled by a spring so stiff that when, at any time, it has very nearly the whole energy of the system, its extreme excursions on each side of its position of equilibrium are small :

"C and A, equal masses :

"C, unacted upon by force except when it strikes L, a fixed barrier, and when it strikes or is struck by B :

"A, unacted on by force except when it strikes or is struck by B, and when it is at less than a certain distance, HK, from a fixed repellent barrier, K, repelling with a force, F, varying according to any law, or constant, when A is between K and H, but becoming infinitely great when (if at any time) A reaches K, and goes infinitesimally beyond it.

"Suppose now A, B, C to be all moving to and fro. The collisions between B and the equal bodies A and C on its two sides must equalize, and keep equal, the average kinetic energy of A, immediately before and after these collisions, to the average kinetic energy of C. Hence, when the times of A being in the space between H and K are included in the average, the average of the *sum of the potential and kinetic energies* of A is equal to the average kinetic energy of C. But the potential energy of A at every point in the space HK is positive, because, according to our supposition, the velocity of A is diminished during every time of its motion from H towards K, and increased to the same value again during motion from K to H. Hence, the average kinetic energy of A is less than the average kinetic energy of C!"

The apparent disproof of the law of partition of energy in this simple problem seems to have shaken the faith even of such experts as Dr. Watson and Mr. Burbury\*. M. Poincaré, however, considering a special case of Lord Kelvin's problem †, arrives at a conclusion in harmony with Maxwell's law. Prof. Bryan‡ considers that the test-case "shows the impossibility of drawing general conclusions as to the distribution of energy in a *single* system from the possible law of permanent distribution in a large number of systems." It is indeed true that Maxwell's theorem relates in the first instance to a large number of systems; but, as I shall show more fully later, the extension to the time-average for a single system requires *only* the application of Maxwell's assumption that all *phases*, i. e. all states, defined both in respect to configuration and velocity, which are consistent with the energy condition

\* Nature, vol. xlvi. p. 100 (1892).

† *Revue générale des Sciences*, July 1894.

‡ "Report on Thermodynamics," Part II. § 26. Brit. Ass. Rep. 1894.

lie on the same path, *i. e.* are attained by the system in its free motion sooner or later. This fundamental assumption, though certainly untrue in special cases, would appear to apply in Lord Kelvin's problem; and, if so, Maxwell's argument requires the equality of kinetic energies for A and C in the time-averages of a *single* system.

In view of this contradiction we may infer that there must be a weak place in one or other argument; and I think I can show that Lord Kelvin's conclusion above that the average of the sum of the potential and kinetic energies of A is equal to the average kinetic energy of C, is not generally true. In order to see this let us suppose the repulsive force F to be limited to a very thin stratum at H, so that A after penetrating this stratum is subject to no further force until it reaches the barrier K; and let us compare two cases, the whole energy being the same in both.

In case (i.) F is so powerful that with whatever velocity (within the possible limits) A can approach, it is reflected at H, which then behaves like a fixed barrier. In case (ii.) F is still powerful enough to produce this result, except when A approaches it with a kinetic energy nearly equal to the whole energy of the system. A then penetrates beyond H, moving slowly from H to K and back again from K to H, thus remaining for a relatively long time beyond H. Lord Kelvin's statement requires that the average total energy of A should be the same in the two cases; but this it cannot be. For during the occasional penetrations beyond H in case (ii.) A has nearly the whole energy of the system; and its enjoyment of this is *prolonged* by the penetration. Hence in case (ii.) A has a higher average total energy than in case (i.); and a margin is provided which may allow the average *kinetic* energies to be equal. I believe that the consideration here advanced goes to the root of the matter, and shows why it is that the possession of potential energy may involve no deduction from the full share of kinetic energy.

Lord Kelvin's "decisive test-case" is entirely covered by Maxwell's reasoning—a reasoning in my view substantially correct. It would be possible, therefore, to take this case as a typical example in illustration of the general argument; but I prefer for this purpose, as somewhat simpler, another test-case, also proposed by Lord Kelvin. This is simply that of a particle moving in two dimensions; and it may be symbolized by the motion of the ball upon a billiard-table. If there is to be potential energy, the table may be supposed to be out of level. The reconsideration of this problem may perhaps be thought superfluous, seeing that it has been ably treated

already by Prof. Boltzmann\*. But his method, though (I believe) quite satisfactory, is somewhat special. My object is rather to follow closely the steps of the general theory. If objections are taken to the argument of the particular case, they should be easy to specify. If, on the other hand, the argument of the particular case is admitted, the issue is much narrowed. I shall have occasion myself to make some comments relating to one point in the general theory not raised by the particular case.

In the general theory the coordinates † of the system at time  $t$  are denoted by  $q_1, q_2, \dots, q_n$ , and the momenta by  $p_1, p_2, \dots, p_n$ . At an earlier time  $t'$  the coordinates and momenta of the same motion are represented by corresponding letters accented, and the first step is the establishment of the theorem usually, if somewhat enigmatically, expressed

$$dq'_1 dq'_2 \dots dq'_n dp'_1 dp'_2 \dots dp'_n = dq_1 dq_2 \dots dq_n dp_1 dp_2 \dots dp_n. \quad \dots \quad (1)$$

In the present case  $q_1, q_2$  are the ordinary Cartesian coordinates ( $x, y$ ) of the particle; and if we identify the mass with unity,  $p_1, p_2$  are simply the corresponding velocity-components ( $u, v$ ); so that (1) becomes

$$dx' dy' du' dv' = dx dy du dv. \quad \dots \quad (2)$$

For the sake of completeness I will now establish (2) *de novo*.

In a possible motion the particle passes from the phase  $(x', y', u', v')$  at time  $t'$  to the phase  $(x, y, u, v)$  at time  $t$ . In the following discussion  $t'$  and  $t$  are absolutely fixed times, but the other quantities are regarded as susceptible of variation. These variations are of course not independent. The whole motion is determined if either the four accented, or the four unaccented, symbols be given. Either set may therefore be regarded as definite functions of the other set. Or again, the four coordinates  $x', y', x, y$  may be regarded as independent variables, of which  $u', v', u, v$  are then functions.

The relations which we require are readily obtained by means of Hamilton's principal function  $S$ , where

$$S = \int_{t'}^t (T - V) dt. \quad \dots \quad (3)$$

In this  $V$  denotes the potential energy in any position, and  $T$

\* Phil. Mag. vol. xxxv. p. 156 (1893).

† Generalized coordinates appear to have been first applied to these problems by Boltzmann.

is the kinetic energy, so that

$$T = \frac{1}{2} u^2 + \frac{1}{2} v^2 = \frac{1}{2} \dot{x}^2 + \frac{1}{2} \dot{y}^2. \quad \dots \quad (4)^*$$

$S$  may here be regarded as a function of the initial and final coordinates; and we proceed to form the expression for  $\delta S$  in terms of  $\delta x'$ ,  $\delta y'$ ,  $\delta x$ ,  $\delta y$ . By (3)

$$\delta S = \int_{t'}^t (\delta T - \delta V) dt, \quad \dots \quad (5)$$

and

$$\begin{aligned} \int \delta T dt &= \int (\dot{x} \delta \dot{x} + \dot{y} \delta \dot{y}) dt \\ &= \int \left( \dot{x} \frac{d \delta x}{dt} + \dot{y} \frac{d \delta y}{dt} \right) dt \\ &= \left[ \dot{x} \delta x + \dot{y} \delta y \right]_{t'}^t - \int (\ddot{x} \delta x + \ddot{y} \delta y) dt; \end{aligned}$$

so that

$$\delta S = \left[ \dot{x} \delta x + \dot{y} \delta y \right]_{t'}^t - \int_{t'}^t (\ddot{x} \delta x + \ddot{y} \delta y + \delta V) dt.$$

By the general equation of dynamics the term under the integral sign vanishes throughout, and thus finally

$$\delta S = u \delta x + v \delta y - u' \delta x' - v' \delta y'. \quad \dots \quad (6)$$

In the general theory the corresponding equation is

$$\delta S = \sum p \delta q - \sum p' \delta q'. \quad \dots \quad (7)$$

Equation (6) is equivalent to

$$\left. \begin{aligned} u' &= -dS/dx', & u &= dS/dx, \\ v' &= -dS/dy', & v &= dS/dy. \end{aligned} \right\}. \quad \dots \quad (8)$$

It is important to appreciate clearly the meaning of these equations.  $S$  is in general a function of  $x$ ,  $y$ ,  $x'$ ,  $y'$ ; and (*e.g.*) the second equation signifies that  $u$  is equal to the rate at which  $S$  varies with  $x$ , when  $y$ ,  $x'$ ,  $y'$  are kept constant, and so in the other cases.

We have now to consider, not merely a single particle, but an immense number of similar particles, moving independently of one another under the same law ( $V$ ), and distributed at time  $t$  over all possible phases ( $x$ ,  $y$ ,  $u$ ,  $v$ ). The

\* As is not unusual in the integral calculus, we employ the same symbols  $x$ , &c. to denote the current and the final values of the variables. If desired, the final values may be temporarily distinguished as  $x''$ , &c.

most general expression for the law of distribution is

$$f(x, y, u, v) dx dy du dv, \dots \quad (9)$$

signifying that the number of particles to be found at time  $t$  within a prescribed range of phase is to be obtained by integrating (9) over the range in question. But such a distribution would in general be *unsteady*. If it obtained at time  $t$ , it would be departed from at time  $t'$ , and *vice versa*, owing to the natural motions of the particles. The question before us is to ascertain what distributions are steady, *i. e.* are maintained unaltered notwithstanding the motions.

It will be seen that it is the spontaneous passage of a particle from one phase to another that limits the generality of the function  $f$ . If there be no possibility of passage, say, from the phase  $(x', y', u', v')$  to the phase  $(x, y, u, v)$ , or, as it may be expressed, if these phases do not lie upon the same *path*, then there is no relation imposed upon the corresponding values of  $f$ . An example, given by Prof. Bryan (*l. c.* § 17), well illustrates this point. Suppose that  $V=0$ , so that every particle pursues a straight course with uniform velocity. The phases  $(x', y', u', v')$  and  $(x, y, u, v)$  can lie upon the same path only if  $u'=u$ ,  $v'=v$ . Accordingly  $f$  remains arbitrary so far as regards  $u$  and  $v$ . For instance, a distribution

$$f(u, v) dx dy du dv \dots \quad (10)$$

is permanent whatever may be the form of  $f$ , understood to be independent of  $x$  and  $y$ . In this case the distribution is *uniform* in space, but uniformity is not indispensable. Suppose, for example, that all the particles move parallel to  $x$ , so that  $f$  vanishes unless  $v=0$ . The general form (9) now reduces to

$$f(x, y, u) dx dy du; \dots \quad (11)$$

and permanency requires that the distribution be uniform along any line for which  $y$  is constant. Accordingly,  $f$  must be independent of  $x$ , so that permanent distributions are of the form

$$f(y, u) dx dy du, \dots \quad (12)$$

in which  $f$  is an arbitrary function of  $y$  and  $u$ . If either  $y$  or  $u$  be varied, we are dealing with a different path (in the sense here involved), and there is no connexion between the corresponding values of  $f$ . But if while  $y$  and  $u$  remain constant,  $x$  be varied, the value of  $f$  must remain unchanged, for the different values of  $x$  relate to the same path.

Before taking up the general question in two dimensions, it may be well to consider the relatively simple case of motion in one dimension, which, however, is not so simple but that

it will introduce us to some of the points of difficulty. The particles are supposed to move independently upon one straight line, and the phase of any one of them is determined by the coordinate  $x$  and the velocity  $u$ . At time  $t'$  the phase of a particle will be denoted by  $(x', u')$ , and at time  $t$  the phase of the same particle will be  $(x, u)$ , where  $u$  will in general differ from  $u'$ , since we no longer suppose that  $V$  is constant, but rather that it is variable in a known manner, *i.e.* is a known function of  $x$ . The number of particles which at time  $t$  lie within the limits of phase represented by  $dx du$  is  $f(x, u) dx du$ , and the question is whether this distribution is steady, and in particular whether it was the same at time  $t'$ . In order to find the distribution at time  $t'$ , we regard  $x, u$  as known functions of  $x', u'$ , and transform the multiple differential. The result of this transformation is best seen by comparison with intermediate transformations in which  $dx du$  and  $dx' du'$  are compared with  $dx dx'$ . We have

$$dx du = dx dx' \times \frac{du}{dx'}, \quad \dots \quad (13)$$

$$dx' du' = dx dx' \times \frac{du'}{dx} \quad \dots \quad (14)$$

In  $du/dx'$  of (13)  $x$  is to be kept constant, and in  $du'/dx$  of (14)  $x'$  is to be kept constant. If we disregard algebraic sign, both are by (8) equal to  $d^2S/dx dx'$ , and are therefore equal to one another. Hence we may write

$$dx du = dx' du'; \quad \dots \quad (15)$$

and the transformation is expressed by

$$f(x, u) dx du = f_1(x', u') dx' du', \quad \dots \quad (16)$$

where  $f_1(x', u')$  is the result of substituting for  $x, u$  in  $f(x, u)$  their values in terms of  $x', u'$ . The right-hand member of (16) expresses the distribution at time  $t'$  corresponding to the distribution at time  $t$  expressed by the left-hand member, as determined by the laws of motion between the two phases. If the distribution is to be steady,  $f_1(x', u')$  must be identical with  $f(x', u')$ ; in other words  $f(x, u)$  must be such a function of  $(x, u)$  that it remains unchanged when  $(x, u)$  refers to various phases of the motion of the same particle. Now, if  $E$  denote the total energy, so that

$$E = \frac{1}{2}u^2 + V, \quad \dots \quad (17)$$

then  $E$  remains constant during the motion; and thus, if for the moment we suppose  $f$  expressed in terms of  $E$  and  $x$ , we

see that  $x$  cannot enter, or that  $f$  is a function of  $E$  only. The only permanent distributions accordingly are those included under the form

$$f(E) dx du, \dots \dots \dots \quad (18)$$

where  $E$  is given by (17), and  $f$  is an arbitrary function.

It is especially to be noticed that the limitation to the form (18) holds only for phases lying upon the same path. If two phases have different energies, they do not lie upon the same path, but in this case the independence of the distributions in the two phases is already guaranteed by the form of (18). The question is whether all phases of *given energy* lie upon the same path. It is easy to invent cases for which the answer will be in the negative. Suppose, for example, that there are two centres of force  $O, O'$  on the line of motion which attract with a force at first proportional to distance but vanishing when the distance exceeds a certain value less than the interval  $OO'$ . A particle may then vibrate with the same (small) energy either round  $O$  or round  $O'$ ; but the phases of the two motions do not lie upon the same path. Consequently  $f$  is not limited by the condition of steadiness to be the same in the two groups of phases. In all cases steadiness is *ensured* by the form (18); and if all phases of equal energy lie upon the same path, this form is *necessary* as well as sufficient.

All the essential difficulties of the theory appear to be raised by the particular case just discussed, and the reader to whom the subject is new is recommended to give it his careful attention.

In the more general problem of motion in two dimensions the discussion follows a parallel course. In order to find the distribution at time  $t'$  corresponding to (9) at time  $t$ , we have to transform the multiple differential, regarding  $x, y, u, v$  as known functions of  $x', y', u', v'$ . Here again we take the initial and final coordinates  $x, y, x', y'$  as an intermediate set of variables. Thus

$$dx' dy' du' dv' = dx' dy' dx dy \times \left| \begin{array}{cc} du' & dv' \\ \frac{dx}{dx'}, & \frac{dy}{dx'} \end{array} \right|, \dots \dots \quad (19)$$

$$dx dy du dv = dx dy dx' dy' \times \left| \begin{array}{cc} du & dv \\ \frac{du}{dx'}, & \frac{dv}{dx'} \end{array} \right|, \dots \dots \quad (20)$$

$$\left| \begin{array}{cc} du & dv \\ \frac{du}{dy'}, & \frac{dv}{dy'} \end{array} \right|, \dots \dots \quad (20)$$

In the determinants of (19), (20) the motion is regarded as a function of  $x, y, x', y'$ , and the three quantities which do not appear in the denominator of any differential coefficient are to be considered constant. This was also the understanding in equations (8), from which we infer that the two determinants are equal, being each equivalent to

$$\left| \begin{array}{cc} \frac{d^2S}{dx dx'}, & \frac{d^2S}{dx dy'} \\ \frac{d^2S}{dx' dy}, & \frac{d^2S}{dy dy'} \end{array} \right| \dots \dots \dots \quad (21)$$

Hence we may write

$$dx dy du dv = dx' dy' du' dv', \dots \dots \quad (22)$$

an equation analogous to (15). By the same reasoning as was employed for motion in one dimension it follows that, if the distribution is to be steady,  $f(x, y, u, v)$  in (9) must remain constant for all phases which lie upon the same path. A distribution represented by

$$f(E) dx dy du dv, \dots \dots \quad (23)$$

where

$$E = \frac{1}{2}u^2 + \frac{1}{2}v^2 + V, \dots \dots \quad (24)$$

will satisfy the conditions of steadiness whatever be the form of  $f$ ; but this form is only *necessary* under the restriction known as Maxwell's assumption or postulate, viz. that all phases of equal energy lie upon the same path.

It is easy to give examples in which Maxwell's assumption is violated, and in which accordingly steady distributions are not limited to (23). Thus, if no force act parallel to  $y$ , so that  $V$  reduces to a function of  $x$  only, the component velocity  $v$  remains constant for each particle, and no phases for which  $v$  differs lie upon the same path. A distribution

$$f(E, v) dx dy du dv \dots \dots \quad (25)$$

is then steady, whatever function  $f$  may be of  $E$  and  $v$ .

That under the distribution (23) the kinetic energy is equally divided between the component velocities  $u$  and  $v$  is evident from symmetry. It is to be observed that the law of equal partition applies not merely upon the whole, but for every element of area  $dx dy$ , and for every value of the total energy, and at every moment of time. When  $x$  and  $y$  are prescribed as well as  $E$ , the value of the resultant velocity itself is determined by (24).

Another feature worthy of attention is the spacial distribution; and it happens that this is peculiar in the present problem. To investigate it we must integrate (23) with respect to  $u$  and  $v$ ,  $x$  and  $y$  being constant. Since  $x$  and  $y$  are constant,  $V$  is constant; so that, if we suppose  $E$  to lie within narrow limits  $E$  and  $E+dE$ , the resultant velocity  $U$  will lie between limits given by

$$U dU = dE. \quad \dots \quad (26)$$

If we transform from  $u, v$  to  $U, \theta$ , where

$$u = U \cos \theta, \quad v = U \sin \theta, \quad \dots \quad (27)$$

$du dv$  becomes  $U dU d\theta$ ; so that on integration with respect to  $\theta$  we have, with use of (26),

$$2\pi F(E) dE \cdot dx dy. \quad \dots \quad (28)$$

The spacial distribution is therefore *uniform*.

In order to show the special character of the last result, it may be well to refer briefly to the corresponding problem in three dimensions, where the coordinates of a particle are  $x, y, z$  and the component velocities are  $u, v, w$ . The steady distribution corresponding to (23) is

$$f'(E) dx dy dz du dv dw, \quad \dots \quad (29)$$

in which

$$E = \frac{1}{2} U^2 + V = \frac{1}{2} u^2 + \frac{1}{2} v^2 + \frac{1}{2} w^2 + V. \quad \dots \quad (30)$$

Here equation (26) still holds good, and the transformation of  $du dv dw$  is, as is well known,  $4\pi U^2 dU$ . Accordingly (29) becomes

$$4\pi F(E) dE \cdot (2E - 2V)^{\frac{1}{2}} dx dy, \quad \dots \quad (31)$$

no longer uniform in space, since  $V$  is a function of  $x, y$ .

In (31) the density of distribution decreases as  $V$  increases. For the corresponding problem in one dimension (18) gives

$$F(E) dE \cdot (2E - 2V)^{-\frac{1}{2}} dx, \quad \dots \quad (32)$$

so that in this case the density *increases* with increasing  $V$ .

The uniform distribution of the two-dimensional problem is thus peculiar. Although an immediate consequence of Maxwell's equation (41), see (41) below, I failed to remark it in the note before referred to, where I wrote as if a uniform distribution in the billiard-table example required that  $V=0$ . In order to guard against a misunderstanding it may be well to say that the uniform distribution does not necessarily extend over the whole plane. Wherever  $(E-V)$  falls below zero there is of course no distribution.

We have thus investigated for a particle in two dimensions the law of steady distribution, and the equal partition of energy which is its necessary consequence. And we see that “the only assumption necessary to the direct proof is that the system, if left to itself in its actual state of motion, will, sooner or later, pass through every phase which is consistent with the equation of energy” (Maxwell). It will be observed that so far nothing whatever has been said as to time-averages for a single particle. The law of equal partition, as hitherto stated, relates to a large number of particles and to a single moment of time.

The extension to time-averages, the aspect under which Lord Kelvin has always considered the problem, is important, the more as some authors appear to doubt the possibility of such extension. Thus Prof. Bryan (Report, § 11, 1894), speaking of Maxwell’s assumption, writes :—“To discover, if possible, a general class of dynamical systems satisfying the assumption would form an interesting subject for future investigation. It is, however, doubtful how far Maxwell’s law would be applicable to the *time-averages* of the energies in any such system. We shall see, in what follows, that the law of permanent distribution of a very large number of systems is in many cases not unique. Where there is more than one possible distribution it would be difficult to draw any inference with regard to the average distribution (taken with respect to the time) for one system.”

The extension to time-averages appears to me to require nothing more than Maxwell’s assumption, without which the law of distribution itself is only an artificial arrangement, sufficient indeed but not necessary for steadiness. We shall still speak of the particle moving in two dimensions, though the argument is general. It has been shown that at any moment the  $u$ -energy and the  $v$ -energy of the group of particles is the same; and it is evident that the equality subsists if we integrate over any period of time. But if this period be sufficiently prolonged, and if Maxwell’s *assumption be applicable*, it makes no difference whether we contemplate the whole group of particles or limit ourselves to a single member of it. It follows that for a single particle the time-averages of  $u^2$  and  $v^2$  are equal, provided the averages be taken over a sufficient length of time.

On the other hand, if in any case Maxwell’s assumption be untrue, not only is the special distribution unnecessary for steadiness, but even if it be artificially arranged, the law of equal time-averages does not follow as a consequence.

Having now considered the special problem at full—I hope

it may not be thought at undue—length, I pass on to some remarks on the general investigation. This proceeds upon precisely parallel lines, and the additional difficulties are merely those entailed by the use of generalized coordinates. Thus (1) follows from (7) by substantially the same process (given in my former note) that (22) follows from (6). Again, if  $E$  denote the total energy of a system, the distribution

$$f(E)dq_1 \dots dq_n dp_1 \dots dp_n \dots \quad (33)$$

where  $f$  is an arbitrary function, satisfies the condition of permanency; and, if Maxwell's assumption be applicable, it is the *only* form of distribution that can be permanent.

As I hinted before, some of the difficulties that have been felt upon this subject may be met by a fuller recognition of the invariantic character of the expressions. This point has been ably developed by Prof. Bryan, who has given (*loc. cit.* § 14) a formal verification that (33) is unaltered by a change of coordinates. If we follow attentively the process by which (1) is established, we see that in (3) there is no assumption that the system of coordinates is the same at times  $t'$  and  $t$ , and that accordingly we are not tied to one system in (33). Indeed, so far as I can see, there would be no meaning in the assertion that the system of generalized coordinates employed for two different configurations was the same \*.

We come now to the deduction from (33) of Maxwell's law of partition of energy. On this Prof. Bryan (*loc. cit.* § 20, remarks :—"Objections have been raised to this step in Maxwell's work by myself ('Report on Thermodynamics,' Part I. § 44) on the ground that the kinetic energy cannot in general be expressed as the sum of squares of *generalized momenta* corresponding to generalized coordinates of the system, and by Lord Kelvin (*Nature*, Aug. 13, 1891) on the ground that the conclusion to which it leads has no intelligible meaning. Boltzmann (*Phil. Mag.* March 1893) has put the investigation into a slightly modified form which meets the first objection, and which imposes a certain restriction upon the generality of the result. Under this limitation the result is perfectly intelligible, and the second objection is therefore also met." At this point I find myself in disagreement with all the above quoted authorities, and in the position of maintaining the correctness of Maxwell's original deduction.

Prof. Boltzmann considers that "Maxwell committed an

\* It would be like saying that two points lie upon the same curve, when the character of the curve is not defined.

error in assuming that by choosing suitable coordinates the expression for the *vis viva* could always be made to contain only the squares of the momenta." This is precisely the objection which I supposed myself to have already answered in 1892. I wrote, "It seems to be overlooked that Maxwell is limiting his attention to systems *in a given configuration*, and that no dynamics is founded upon the reduced expression for T. The reduction can be effected in an infinite number of ways. We may imagine the configuration in question rendered one of stable equilibrium by the introduction of suitable forces proportional to displacements. The principal modes of isochronous vibration thus resulting will serve the required purpose."

It is possible, therefore, so to choose the coordinates that for a given configuration (and for configurations differing infinitely little therefrom) the kinetic energy T, which is always a quadratic function of the velocities, shall reduce to a sum of squares with, if we please, given coefficients. Thus *in the given configuration*

$$T = \frac{1}{2} \dot{q}_1^2 + \frac{1}{2} \dot{q}_2^2 + \dots + \frac{1}{2} \dot{q}_n^2; \quad \dots \quad \dots \quad (34)$$

and, since in general  $p = dT/d\dot{q}$ ,

$$p_1 = \dot{q}_1, \quad p_2 = \dot{q}_2, \quad \text{&c.,}$$

so that

$$T = \frac{1}{2} p_1^2 + \frac{1}{2} p_2^2 + \dots + \frac{1}{2} p_n^2. \quad \dots \quad \dots \quad (35)$$

Whether the coordinates required to effect a similar reduction for other configurations are the same is a question with which we are not concerned.

The mean value of  $p_r^2$  for all the systems in the given configuration is, according to (33),

$$\frac{\int p_r^2 \cdot F\{V + \frac{1}{2} p_1^2 + \dots + \frac{1}{2} p_n^2\} dp_1 \dots dp_n}{\int F\{V + \frac{1}{2} p_1^2 + \dots + \frac{1}{2} p_n^2\} dp_1 \dots dp_n}. \quad (36)^*$$

The limits for each variable may be supposed to be  $\pm \infty$ ; but the large values do not really enter if we suppose F(E) to be finite for moderate, perhaps for nearly definite, values of E only.

It is now evident that the mean value is the same for all the momenta  $p$ ; and accordingly that for each the mean value of  $\frac{1}{2} p^2$  is  $1/n$  of the mean value of T. This result holds good for every moment of time, for every configuration, for every value of E, and for every system of resolution (of which there

\* Confer Bryan, loc. cit.

are an infinite number) which allows  $T$  to be expressed in the form (35).

In the case where the "system" consists of a single particle, (35) is justified by any system of rectangular coordinates; and although we are not bound to use the same system for different positions of the particle, it would conduce to simplicity to do so. If the system be a rigid body, we may measure the velocities of the centre of inertia parallel to three fixed rectangular axes, while the remaining momenta refer to rotations about the principal axes of the body. If Maxwell's assumption hold good, a permanent distribution is such that in one, or in any number of positions, the mean energy of each rotation and of each translation is the same. And under the same restriction a similar assertion may be made respecting the time-averages for a single rigid body.

There is much difficulty in judging of the applicability of Maxwell's assumption. As Maxwell himself showed, it is easy to find cases of exception; but in most of these the conditions strike one as rather special. It must be observed, however, that if we take it quite literally, the assumption is of a severely restrictive character; for it asserts that the system, starting from any phase, will traverse *every* other phase (consistent with the energy condition) *before* returning to the initial phase. As soon as the initial phase is recovered, a cycle is established, and no new phases can be reached, however long the motion may continue.

We return now to the question of the distribution of momenta among the systems which occupy a given configuration, still supposing the coordinates so chosen as to reduce  $T$  to a sum of squares (35). It will be convenient to fix our attention upon systems for which  $E$  lies within narrow limits,  $E$  and  $E+dE$ . Since  $E$  is given, there is a relation between  $p_1, p_2, \dots, p_n$ , and we may suppose  $p_n$  expressed in terms of  $E$  and the remaining momenta. By (35)

$$p_n dp_n = dT = dE,$$

since the configuration is given, and thus (33) becomes

$$f(E)dE \cdot dq_1 \dots dq_n \cdot p_n^{-1} dp_1 \dots dp_{n-1} \dots \quad \dots \quad (37)$$

For the present purpose the latter factors alone concern us, so that what we have to consider is

$$\frac{dp_1 dp_2 \dots dp_{n-1}}{\sqrt{\{2T - p_1^2 - p_2^2 - \dots - p_{n-1}^2\}}}, \quad \dots \quad (38)$$

in which  $T$ , being equal to  $E - V$ , is given. For the moment we may suppose that  $2T$  is unity.

The whole number of systems is to be found by integrating (38), the integral being so taken as to give the variables all values consistent with the condition that  $p_1^2 + p_2^2 + \dots + p_{n-1}^2$  is not greater than unity. Now

$$\int \dots \int \frac{dp_1 dp_2 \dots dp_{n-1}}{\sqrt{1-p_1^2 - \dots - p_{n-1}^2}} = \frac{\pi^{\frac{1}{2}n-\frac{1}{2}}}{\Gamma(\frac{1}{2}n-\frac{1}{2})} \int_{-1}^{+1} (1-p_1^2)^{\frac{1}{2}n-\frac{3}{2}} dp_1, \quad \dots \quad (39)$$

and

$$\int_{-1}^{+1} (1-p_1^2)^{\frac{1}{2}n-\frac{3}{2}} dp_1 = \frac{\Gamma(\frac{1}{2}) \Gamma(\frac{1}{2}n-\frac{1}{2})}{\Gamma(\frac{1}{2}n)}. \quad \dots \quad (40)$$

in which  $\Gamma(\frac{1}{2}) = \sqrt{\pi}$ . Thus the whole number of systems is

$$\frac{\{\Gamma(\frac{1}{2})\}^n}{\Gamma(\frac{1}{2}n)},$$

or on restoration of  $2T$ , equal to  $2E - 2V$ ,

$$\frac{\{\Gamma(\frac{1}{2})\}^n}{\Gamma(\frac{1}{2}n)} \{2E - 2V\}^{\frac{1}{2}n-1}. \quad \dots \quad (41)$$

To this we shall return later; but for the present what we require to ascertain is the distribution of one of the momenta, say  $p_1$ , irrespectively of the values of the remaining momenta. By (39), (40) the number of systems for which  $p_1$  lies between  $p_1$  and  $p_1 + dp_1$  in comparison with the whole number of systems is

$$\frac{\Gamma(\frac{1}{2}n)}{\Gamma(\frac{1}{2}) \Gamma(\frac{1}{2}n-\frac{1}{2})} \left\{ 1 - \frac{p_1^2}{2T} \right\}^{\frac{1}{2}n-\frac{3}{2}} \frac{dp_1}{\sqrt{(2T)}}. \quad \dots \quad (42)$$

This is substantially Maxwell's investigation, and (42) corresponds with his equation (51). As was to be expected, the law of distribution is the same for all the momenta. From the manner of its formation, we note that the integral of (42), taken between the limits  $p_1 = \pm \sqrt{(2T)}$ , is equal to unity.

Maxwell next proceeds to the consideration of the special form assumed by (42), when the number  $n$  of degrees of freedom is extremely great \*. This part of the work seems to be very important; but it has been much neglected, probably because the result was not correctly stated.

Dropping the suffix as unnecessary, we have to consider the form of

$$\left\{ 1 - \frac{p^2}{2T} \right\}^{\frac{1}{2}n-\frac{3}{2}}$$

when  $n$  is very great, the mean value of  $p^2$  becoming at the

\* The particular cases where  $n=2$ , or  $n=3$ , are also worthy of notice.

same time small in comparison with  $2T$ . If we write

$$T = nK = \frac{1}{2}nP^2, \dots \dots \dots \quad (43)$$

we have

$$\text{Limit } \left\{ 1 - \frac{p^2}{2T} \right\}^{\frac{1}{2}n-\frac{3}{2}} = e^{-p^2/4K} = e^{-p^2/2P^2}. \dots \quad (44)$$

The limit of the fraction containing the  $\Gamma$  functions may be obtained by the formula

$$\Gamma(m+1) = e^{-m} m^m \sqrt{(2m\pi)};$$

and the limiting form of (42) becomes

$$\frac{e^{-p^2/4K}}{\sqrt{(2\pi)}} \frac{dp}{\sqrt{(2K)}}, \text{ or } \frac{e^{-p^2/2P^2}}{\sqrt{(2\pi)}} \frac{dp}{P}. \dots \quad (45)$$

It may be observed that the integral of (45) between the limits  $\pm\infty$  is unity, and that this fact might have been used to determine the numerical factor.

Maxwell's result is given in terms of a quantity  $k$ , analogous to  $K$ , and defined by

$$\frac{1}{2}p^2 = k. \dots \dots \dots \quad (46)$$

It is

$$\frac{1}{\sqrt{(2\pi)}} \frac{1}{K} e^{-\frac{k}{2K}} dk. \dots \dots \dots \quad (47)$$

The corresponding form from (45) is

$$\frac{1}{\sqrt{(2\pi)}} \frac{1}{2\sqrt{(kK)}} e^{-\frac{k}{2K}} dk. \dots \dots \dots \quad (48)$$

In like manner if we inquire what proportion of the whole number of systems have momenta lying within the limits denoted by  $dp_1 dp_2 \dots dp_r$ , where  $r$  is a number very small relatively to  $n$ , we get

$$e^{-(p_1^2 + p_2^2 + \dots + p_r^2)/4K} \frac{dp_1 dp_2 \dots dp_r}{\{\sqrt{(2K)}\}^r}, \dots \quad (49)$$

or, if we prefer it,

$$\frac{e^{-(p_1^2 + p_2^2 + \dots + p_r^2)/2P^2}}{\{\sqrt{(2\pi)}\}^r} \frac{dp_1 dp_2 \dots dp_r}{P^r}. \dots \quad (50)$$

These results follow from the general expression (38), in the same way as does (45), by stopping the multiple integration at an earlier stage. The remaining variables range over values which may be considered in each case to be unlimited.

If the integration between  $\pm\infty$  be carried out completely, we recover the value unity.

The interest of the case where  $n$  is very great lies of course in the application to a gas supposed to consist of an immense number of similar molecules\*, or of several sets of similar molecules; and the question arises whether (45) can be applied to deduce the Maxwellian law of distribution of velocities among the molecules of a single system at a given instant of time. A caution may usefully be interposed here as to the sense in which the Maxwellian distribution is to be understood. It would be absurd to attempt to prove that the distribution in a single system is necessarily such and such, for we have already assumed that every phase, including every distribution of velocities, is attainable, and indeed attained if sufficient time be allowed. The most that can be proved is that the distribution will *approximate* to a particular law for the greater part of the time, and that if sensible deviations occur they will be *transitory*.

In applying (45) to a gas it will be convenient to suppose in the first instance that all the molecules are similar. Each molecule has several degrees of freedom, but we may fix our attention upon one of them, say the  $x$ -velocity of the centre of inertia, usually denoted by  $u$ . In (45) the *whole* system is supposed to occupy a given configuration; and the expression gives us the distribution of velocity at a given time for a single molecule among all the systems. The distribution of velocity is the same for every other molecule, and thus the expression applies to the statistics of all the molecules of all the systems. Does it also apply to the statistics of all the molecules of a single system? In order to make this inference we must assume that the statistics are the same (at the same time) for all the systems, or, what comes to the same thing (if Maxwell's assumption be allowed), that they are the same for the same system at the various times when it passes through a given configuration.

Thus far the argument relates only to a single configuration. If the configuration be changed, there will be in general a change of potential energy and a corresponding change in the kinetic energy to be distributed amongst the degrees of freedom. But in the case of a gas, of which the statistics are assumed to be regular, the potential energy remains approximately constant when exclusion is made of exceptional conditions. The same law of distribution of velocity then applies to every configuration, that is, it may be asserted

\* The terms "gas" and "molecule" are introduced for the sake of brevity. The question is still purely dynamical.

without reference to the question of configuration. We thus arrive at the Maxwellian law of velocities in a single gas, as well as the relation between the velocities in a mixture of molecules of different kinds first laid down by Waterston.

The assumptions which we have made as to the practical regularity of statistics are those upon which the usual theory of ideal gases is founded; but the results are far more general. Nothing whatever has been said as to the character of the forces with which the molecules act upon one another, or are acted upon by external agencies. Although for distinctness a gas has been spoken of, the results apply equally to a medium constituted as a liquid or a solid is supposed to be. A kinetic theory of matter, as usually understood, appears to require that in equilibrium the whole kinetic energy shall be equally shared among all the degrees of freedom, and within each degree of freedom be distributed according to the same law. It is included in this statement that temperature is a matter of kinetic energy only, *e.g.* that when a vertical column of gas is in equilibrium, the mean velocity of a molecule is the same at the top as at the bottom of the column.

Reverting to (37), (41), in order to consider the distribution of the systems as dependent upon the coordinates independently of the velocities, we have, omitting unnecessary factors,

$$\{E - V\}^{\frac{1}{2}n-1} dq_1 dq_2 \dots dq_n. \dots \quad (51)$$

If  $n=2$ , *e.g.* in the case already considered of a single particle moving in two dimensions, or of two particles moving in one dimension, or again whatever  $n$  may be, provided  $V$  vanish, the first factor disappears, so that the distribution is *uniform* with respect to the coordinates  $q_1 \dots q_n$ . If  $n > 2$  and  $V$  be finite, the distribution is such as to favour those configurations for which  $V$  is least.

"When the number of variables is very great, and when the potential energy of the specified configuration is very small compared with the total energy of the system, we may obtain a useful approximation to the value of  $\{E - V\}^{\frac{1}{2}n-1}$  in an exponential form; for if we write (as before)  $E = nK$ ,

$$\{E - V\}^{\frac{1}{2}n-1} = E^{\frac{1}{2}n-1} e^{-V/2K} \dots \dots \quad (52)$$

nearly, provided  $n$  is very great and  $V$  is small compared with  $E$ . The expression is no longer approximate when  $V$  is nearly as great as  $E$ , and it does not vanish, as it ought to do, when  $V = E$ ." (Maxwell).

In the case of gas composed of molecules whose mutual influence is limited to a small distance and which are not subject to external forces, the distribution expressed by (51)

is uniform in space except near the boundary. For if  $q_1$  denote the  $x$ -coordinate of a particular molecule, and if we effect the integration with respect to all the coordinates of other molecules as well as the other coordinates of the particular molecule, we must arrive at a result independent of  $x$ , provided  $x$  relate to a point well in the interior. That is to say in the various systems contemplated the particular molecule is uniformly distributed with respect to  $x$ . The same is true of  $y$  and  $z$ , and thus the whole spacial distribution is uniform. If the single system constituting the gas has uniform statistics, it will follow that the distribution in it of molecules similar to the particular molecule is uniform.

The uniformity of the distribution is disturbed if an external force acts. In illustration of this we may consider the case of gravity. From (52) the distribution with respect to the coordinates of the particular molecule will be

$$e^{-gz/2K} dx dy dz,$$

and the same formula gives the density of molecules similar to the particular molecule in a single system.

The main purpose of this paper is now accomplished ; but I will take the opportunity to make a few remarks upon some general aspects of a kinetic theory of matter. Many writers appear to commit themselves to absolute statements, but Kelvin\* and Boltzmann and Maxwell fully recognize that conclusions can never be more than *probable*. The second law of thermodynamics itself is in this predicament. Indeed it might seem at first sight as if the case were even worse than this. Mr. Culverwell has emphasized a difficulty, which must have been pretty generally felt, arising out of the reversibility of a dynamical system. If during one motion of a system energy is dissipated, restoration must occur when the motion is reversed. How then is one process more probable than the other? Prof. Boltzmann has replied to this objection, upon the whole I think satisfactorily, in a very interesting letter †. The available (internal) energy of a system tends to zero, or

\* Witness the following remarkable passage :—"It is a strange but nevertheless a true conception of the old well-known law of the conduction of heat to say that it is very improbable that in the course of 1000 years one-half the bar of iron shall of itself become warmer by a degree than the other half: and that the probability of this happening before 1,000,000 years pass is 1000 times as great as that it will happen in the course of 1000 years, and that it certainly will happen in the course of some very long time."—('Nature,' vol. ix. p. 443, 1874.)

† 'Nature,' vol. li. p. 413 (1895).

rather to a small value, only because the conditions, or phases as we have called them, corresponding to small values are more probable, *i.e.* more numerous. If there is considerable available energy at any moment, it is because the condition is then exceptional and peculiar. After a short interval of time the condition *may* become more peculiar still, and the available energy *may* increase, but this is improbable. The probability is that the available energy will, if not at once, at any rate after a short interval, decrease owing to the substitution of a more nearly normal state of things.

There is, however, another side to this question, which perhaps has been too much neglected. Small values of the available energy are indeed more probable than large ones, but there is a degree of smallness below which it is *improbable* that the value will lie. If at any time the value lies extremely low, it is an increase and not a decrease which is probable. Maxwell showed long ago how a being capable of dealing with individual molecules would be in a position to circumvent the second law. It is important to notice that for this end it is not necessary to deal with individual molecules. It would suffice to take advantage of local reversals of the second law, which will involve, not very rarely, a *considerable number* of neighbouring molecules. Similar considerations apply to other departures from a normal state of things, such, for example, as unequal mixing of two kinds of molecules, or such a departure from the Waterston relation (of equal mean kinetic energies) as has been investigated by Maxwell and by Tait and Burbury.

The difficulties connected with the application of the law of equal partition of energy to actual gases have long been felt. In the case of argon and helium and mercury vapour the ratio of specific heats (1·67) limits the degrees of freedom of each molecule to the three required for translatory motion. The value (1·4) applicable to the principal diatomic gases gives room for the three kinds of translation and for two kinds of rotation. Nothing is left for rotation round the line joining the atoms, nor for relative motion of the atoms in this line. Even if we regard the atoms as mere points, whose rotation means nothing, there must still exist energy of the last-mentioned kind, and its amount (according to the law) should not be inferior.

We are here brought face to face with a fundamental difficulty, relating not to the theory of gases merely, but rather to general dynamics. In most questions of dynamics a condition whose violation involves a large amount of potential energy may be treated as a *constraint*. It is on this

principle that solids are regarded as rigid, strings as inextensible, and so on. And it is upon the recognition of such constraints that Lagrange's method is founded. But the law of equal partition disregards potential energy. However great may be the energy required to alter the distance of the two atoms in a diatomic molecule, practical rigidity is never secured, and the kinetic energy of the relative motion in the line of junction is the same as if the tie were of the feeblest. The two atoms, however related, remain two atoms, and the degrees of freedom remain six in number.

What would appear to be wanted is some escape from the destructive simplicity of the general conclusion relating to partition of kinetic energy, whereby the energy of motions involving larger amounts of potential energy should be allowed to be diminished in consequence. If the argument, as above set forth after Maxwell, be valid, such escape must involve a repudiation of Maxwell's fundamental postulate as practically applicable to systems with an immense number of degrees of freedom.

**VII. On Swan's Prism Photometer, commonly called Lummer and Brodhun's Photometer. By Prof. C. G. KNOTT, D.Sc.\*.**

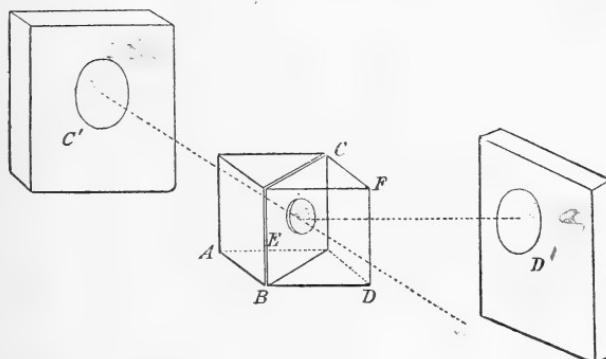
**I**N 1849 William Swan, subsequently Professor of Natural Philosophy in the University of St. Andrews, read a paper "On the Gradual production of Luminous Impressions on the Eye and other Phenomena of Vision" before the Royal Society of Edinburgh (see *Transactions*, vol. xvi.). This paper contains some results of high interest, but I have no recollection of ever having seen it referred to in modern literature on the subject.

On April 4, 1859, Professor Swan gave a second paper on the same subject, much briefer than the first, and entirely occupied with descriptions of greatly improved forms of apparatus (see *Transactions*, vol. xxii.). Among the forms of apparatus described is his "Prism Photometer." This is simply and solely the form of photometer described in 1889, exactly thirty years later, by Lummer and Brodhun, and named after them in all recent literature (see *Zeitschrift für Instrumentenkunde*, Bd. ix.). I cannot do better than give Swan's description in full, and reproduce his own diagram.

He writes:—"An arrangement which, from an imperfect

\* Communicated by the Author: read before the Royal Society of Edinburgh, Dec. 17th, 1899.

trial I have made of it, promises to succeed well for comparing the brightness of the illuminated apertures, may be made by cementing together two equal and similar rectangular glass prisms A B C, B C D, so as to form a parallelopiped, by means of a small portion of Canada balsam, which, when the prisms are pressed together, expands into a circular thin film E. The illuminated apertures C', D' in the screens are



placed opposite to the faces A C, C D, and the observer looks through the face B F. The light transmitted through A C, and falling on B C, will be totally reflected, except the portion which falls on the film of Canada balsam at E, which will be nearly all transmitted to the eye of the observer. The light which is transmitted through the face C D will be totally reflected to the eye by the face B C, except what falls on the Canada balsam at E, which will be nearly all transmitted. The spot E will appear of a different brightness from the rest of the surface B C, except when the light totally reflected by B C is equal in intensity to the sum of the lights transmitted and reflected at E. The spot E will then disappear, owing to the whole surface of B C, including the spot, becoming uniformly bright. Assuming that the light partially reflected at E has a constant ratio to that totally reflected by the rest of the surface B C, and to that transmitted by A C, it is obvious that the squares of the distances of the flame from the aperture D' when the spot E disappears will give the ratio of the intensities of the lights transmitted by the aperture C'."

Swan's intention was to publish the results obtained with his improved apparatus; but we can find no record of the continuation of the work. Probably he obtained nothing that materially added to or in any way affected the accuracy

of his earlier results ; and it was not his habit to write for mere writing's sake.

But whatever may have been the real reason for his subsequent silence, there is not the least doubt that Swan invented, described, constructed, and used, thirty years before the scientific world was ready for it, the prism-photometer which Lummer and Brodhun had to re-invent. One of the photometers constructed by Swan himself is now among the apparatus of the Physical Laboratory of Edinburgh University, having been purchased by Professor Tait some years ago along with the best part of Professor Swan's private collection. This photometer is in regular use in the Laboratory.

In the same collection were also two other small prisms intended for the same purpose, but not made up. The lid of the small box containing them still bears the inscription in Professor Swan's own handwriting :—"Pair of fine plate-glass prisms made for me by Cooke (1870) for my prism-photometer." This inscription, written fully ten years after the first published description, shows that Swan was in the habit of using his photometer.

The fact that Swan had forestalled Lummer and Brodhun in the invention and construction of an ingenious form of photometer has of course been familiar to all officially connected with the Edinburgh University Physical Laboratory for some years past. Recently, having occasion to enquire somewhat closely into the history of photometric methods, I determined to make a systematic search through Swan's published papers, which for the most part treat of optical subjects. I had not far to search ; for on the plate illustrating the second paper named above I recognized at a glance the prism-photometer, and immediately thereafter discovered the descriptive paragraph. My expectation at most was to find some incidental reference to the instrument. To my surprise I found as complete a description of the *essential* instrument as anyone could desire to find. It will remain always a matter of no small astonishment that such an important contribution to knowledge should have escaped the notice of the myriad workers in photometry. In Swan's day there was not the same great interest taken in the subject ; but that is no excuse for present neglect.

Swan's photometer was given to a world not ready for its reception. Let us now, who know its value, not forget that it is "Swan's" photometer.

**VIII. The Magnetic Properties of the Alloys of Iron and Aluminium.—PART I.** By S. W. RICHARDSON, D.Sc., late 1851 Exhibition Research Scholar; Lecturer and Demonstrator in Physics at the University College, Nottingham\*.

CONTENTS.

- § I. The Introduction.
- § II. A discussion of the method used for the magnetic measurements, and a description of the apparatus.
- § III. An account of the method used for determining the temperature.
- § IV. An account of the methods used for varying the temperature.
- § V. The data obtained and some remarks upon them.

§ I. THE INTRODUCTION.

THE experiments made by Hopkinson† on alloys of iron and nickel led to such striking results that the author thought that experiments of the same nature on other alloys of iron might contribute some interesting facts to our knowledge of Magnetism. Accordingly a series of experiments were undertaken on some alloys of iron and aluminium. An account of the earlier experiments on these alloys, performed at the Cavendish Laboratory during the years 1897 and 1898, is given in this paper; the later experiments being reserved for a subsequent communication.

The alloys were made to the author's order by the British Aluminium Company. Considerable difficulty was experienced at first in obtaining satisfactory specimens, the ones first made being very brittle and liable to split when smartly struck. This was no doubt due mainly to rapid cooling. After taking suitable precautions against this, however, sufficiently durable specimens were obtained—unless the amount of aluminium approached 30 per cent., in which case the alloys gradually disintegrated to fine powder with the evolution of acetylene gas.

The specimens actually investigated contained 3·64, 5·44, 9·89, and 18·47 per cent. of aluminium respectively. The first was comparatively soft and could easily be turned in a lathe; but the other three (in which the carbon was in the combined form) were extremely hard, and it was found impossible to cut them with ordinary tools. The rings used in the experiments were obtained by casting the metal into a disk and boring out the central part of this by means of a rotating copper tube fed with emery-powder and oil.

\* Communicated by the Physical Society: read October 27, 1899.

† 'Proceedings of the Royal Society,' December 1889, January and May 1890.

The experiments made extend over temperatures ranging from  $-83^{\circ}$  C. to  $+900^{\circ}$  C.

To obtain the low temperatures, the specimen, wound with primary and secondary coils, was immersed in an ether bath surrounded by a cooling medium of either ice and salt or carbon-dioxide snow. The ether bath was connected with a water-pump, by means of which rapid evaporation could be set up, and the ether thus cooled below the temperature of the surrounding medium.

The carbon-dioxide snow was obtained from Guinness's brewery, Dublin, and was sent over in a barrel packed with cowhair. Although the journey took three days, the loss due to evaporation was comparatively small, being not more than one quarter of the whole amount. While working with the carbon-dioxide snow the experiments were continued throughout the night, and on one occasion the author conducted an experiment for 36 consecutive hours.

The high temperatures were obtained by means of Fletcher's improved muffle-furnace, furnished with a governor to regulate the supply of gas to the furnace. In later experiments, however, the alloys have been heated electrically by an arrangement similar to that used by Morris\* in his experiments on the magnetic properties of iron. This method has been found to be in every respect superior to the furnace method.

The temperatures were deduced from the resistance of the secondary coil, which was of platinum wire, and was wound next to the ring.

The chief results obtained from the experiments recorded in this paper may be summed up generally as follows :—

(1) The alloys behave magnetically as though they consisted of two distinct media superposed.

(2) The general roundness of the curves and their lack of abruptness near the critical point seem to indicate that the alloys are heterogeneous in structure. A similar lack of abruptness near the critical point will be seen in the curves obtained by Hopkinson for nickel-iron alloys.

(3) The permeability decreases with rise of temperature near the critical point until a minimum value is reached, when further rise of temperature produces very slight diminution, if any, in the permeability.

Morris† has shown that in the case of iron we have a remanent permeability after passing the critical point (which result has since been corroborated by Hopkinson ‡).

(4) The experiments suggest that the maximum value of

\* Phil. Mag. Sept. 1897.      † *Loc. cit.*

‡ 'Proceedings of the Royal Society,' 1898.

the permeability for an alloy containing 10 per cent. of aluminium is reached at about  $-90^{\circ}$  C.

(5) An alloy containing 18·47 per cent. of aluminium has a critical point of about  $25^{\circ}$  C., and gives no indication of temperature hysteresis. This alloy probably has a maximum permeability at a temperature much below  $-90^{\circ}$  C.

## § II. THE MAGNETIC MEASUREMENTS.

### *Theory of the Method.*

The ring of metal X (fig. 1) whose magnetic properties are to be investigated is wound with a primary  $P_2$  and a secondary  $S_2$ . The primary is connected in series with a battery B, the primary  $P_1$  of a standard mutual inductance coil Y, an adjustable resistance R, a reversing-key K, and a Weston's ammeter A.

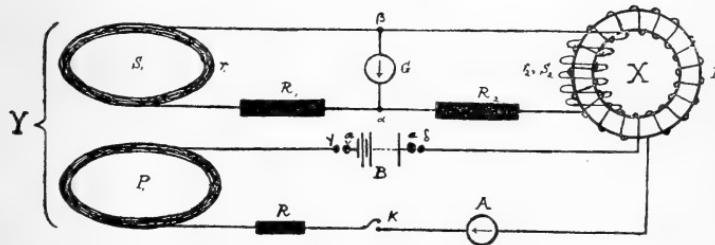
The secondary  $S_2$  is connected in series with the secondary  $S_1$  of the standard mutual inductance-coil Y, and two adjustable noninductive resistances  $R_1$  and  $R_2$ .

One terminal of a galvanometer is connected with the point  $\alpha$  between  $R_1$  and  $R_2$ , and the other terminal with the point  $\beta$  on the opposite side of the bridge.

The secondaries are connected up so that the flows generated in them on reversing the primary are opposed in the branch  $\alpha \beta$ .

The resistances  $R_1$  and  $R_2$  are adjusted until on reversing the primary circuit no quantity of electricity passes through the galvanometer.

Fig. 1.



Then, if

B = the induction in the ring X,

$\sigma$  = the mean sectional area of the ring,

N = the number of turns in the secondary of ring ( $S_2$ ),

$r_2$  = the resistance of  $S_2$ ,

$r_1$  = " " of  $S_1$ ,

M = the mutual inductance of Y,

$\gamma$  = the value of the steady current in the primary circuit;

we have

$$\frac{B \times \sigma \times N}{R_2 + r_2} = \frac{M\gamma}{R_1 + r_1},$$

or

$$B = \frac{M}{\sigma \times N} \frac{R_2 + r_2}{R_1 + r_1} \gamma^*.$$

And if

$H$ =the field strength in the ring X,  
 $n$ =the number of turns in the primary of X,  
 $d$ =the mean diameter of the ring,

$$H \doteq \frac{4n}{d} \gamma.$$

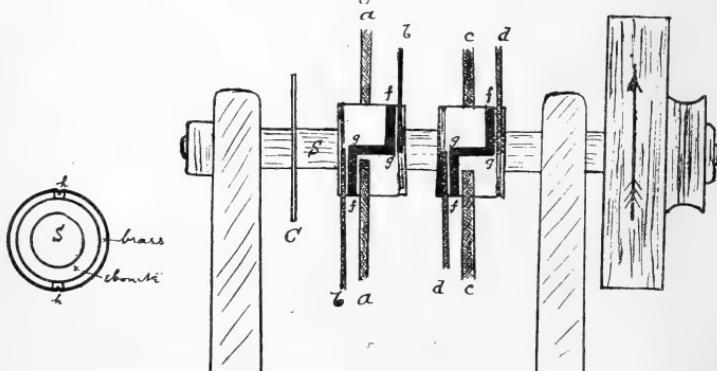
*Note.*—This is the condition for no quantity through the galvanometer. The condition for no current through the galvanometer cannot be satisfied owing to the variability of the permeability with the field strength. It will, however, be seen later that this did not materially affect the experiments.

#### Practice of the Method.

The sensitiveness of the method was increased by means of a secohmmeter making about 3 alternations per second.

The secohmmeter D, a diagram of which is shown in fig. 2, consisted of two ebonite rings fitted on to a steel axle S. To each ebonite ring was attached externally a cylindrical brass ring divided along the black lines f,f.

Fig. 2.



Close to the edges of the brass rings were grooves. In these grooves fitted contacts of copper gauze b, b, d, d. Two other pairs of contacts of copper gauze a, a, c, c, pressed against the central portions of the brass rings. The contact

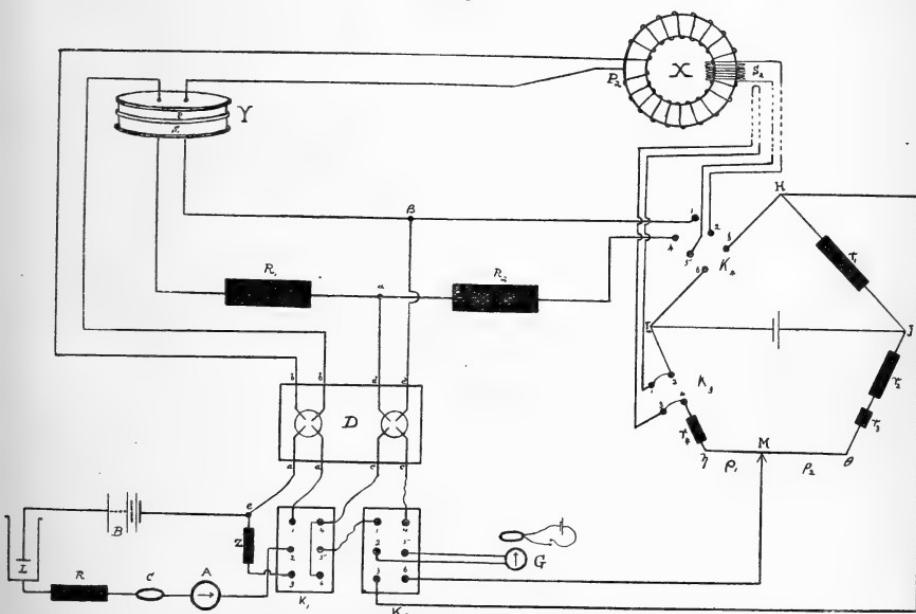
\* Cf. Maxwell, vol. ii. p. 395.

pieces  $a, a$ , were connected to the two terminals of the battery  $B$ , *vide* figs. 1 and 2, and the two terminals  $b, b$ , to the points  $\gamma, \delta$ , in the primary circuit (fig. 1). It will be seen that at each half revolution of the secohmmeter the current in the primary circuit was reversed.

The contact pieces  $c, c$  were connected to the two terminals of the galvanometer  $G$  (figs. 1 and 3), and  $d, d$  to the points  $\alpha, \beta$  in the secondary circuit. The secohmmeter was driven by a small motor, and the contacts were arranged so that the galvanometer connexions were reversed immediately before the reversal of the battery. The direction of rotation is shown by the arrow (fig. 2).

Pieces of ebonite were fitted into the spaces  $g, g$  to allow the central contacts to pass smoothly over them. In time the insulation becomes impaired owing to the continuous deposition of brass on the ebonite. To prevent this, V-shaped grooves  $h, h$  were cut in the ebonite, and thus the continuity of the deposit was broken. These grooves were scraped out from time to time during the experiments.

Fig. 3.



*The Branch Circuit.*—To prevent the heating of the primary coils due to the passage of the current for any lengthened period a branch circuit  $Z$  (fig. 3), whose resistance was equal to that of the primary coils, was made use of.

The brushes  $a\ a$  of the secohmmeter D were joined to the mercury cup 1 of the rocker  $K_1$  and to the point  $e$  respectively. This rocker serves the double purpose of throwing the current in and out of the primaries and of obtaining a zero. This second purpose is considered under a separate heading. The three arms of the rocker on either side are soldered together. In the initial position the points 2 and 3 are connected up, and the current flows through the branch circuit Z. On reversal, the points 1 and 2 are joined, and the current then flows through the primaries of X and Y.

*The Galvanometer.*—The resistance of the galvanometer finally used in the experiments was about 7 ohms. It was made as sensitive as possible. A weighted needle was used in the first experiments, but was afterwards discarded as it was found that the gain in steadiness was more than outbalanced by the loss of sensitiveness. The needle was never absolutely at rest, owing to the difference of the time constants in the two secondaries, and the variability of that of X. This effect was not sufficient to prevent the detection of a deflexion of  $\frac{1}{2}$  millim. on the scale. The scale was read by means of a telescope placed at some distance from the galvanometer. The mutual inductance Y was placed with its axis vertical, and at such a distance from the galvanometer as not to disturb the needle.

*To obtain a Zero.*—The mercury cups 4 and 6 in the key  $K_1$  are connected. On reversing the rocker, the galvanometer is first cut out and then reconnected. The lengths of the legs of the rocker are such that the current is reversed *before* the galvanometer is reconnected. If the rocker be turned over slowly, the spot of light moves off continuously from the zero.

*The Mutual Inductance.*—The coil Y was wound with one primary and three secondaries. The values of the mutual inductances for the separate secondaries were  $9.04 \times 10^6$ ,  $7.014 \times 10^6$ , and  $4.536 \times 10^6$  respectively. It was hence possible to vary considerably the value of the mutual inductance used in the experiments. The values given above were determined by comparison with a standard coil whose mutual inductance had been carefully calculated.

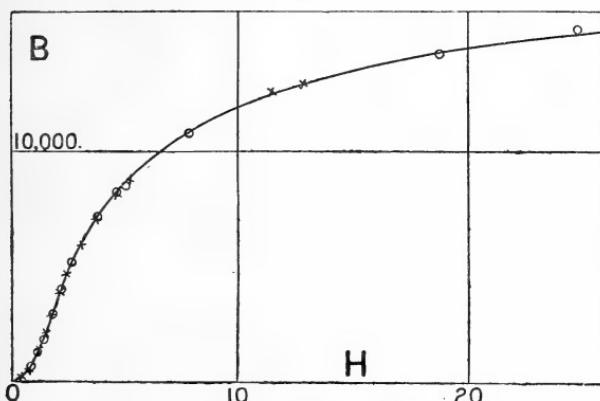
*Comparison with the Ballistic Method.*—It was thought desirable to compare the results obtained by this method with those obtained from one of the methods in common use. For this purpose a laminated iron ring was wound with primary and secondary coils and was compared with the standard inductance ( $= 9.040 \times 10^6$ ), first by the Ballistic Method and secondly by the Balance Method.

The values of the induction obtained in the two sets of experiments are given below.

Ballistic Method.		Balance Method.	
H.	B.	H.	B.
0.97	644	0.52	160
1.24	1,285	0.92	553
1.49	1,870	1.30	1,421
1.85	2,990	1.56	2,190
2.20	4,050	1.81	2,895
2.70	5,230	2.17	3,905
3.90	7,230	2.50	4,730
4.69	8,170	3.13	5,960
5.08	8,470	3.84	7,075
7.82	10,850	4.76	8,150
18.80	14,230	5.40	8,790
24.80	15,150	11.38	12,690
		12.87	13,020
		26.50	15,230

These results are plotted in fig. 4, the ballistic reading being indicated thus  $\circ$ , and the balance readings thus  $\times$ . It will be seen that the two series of results agree with one another within the limits of experimental error.

Fig. 4.



*Eddy Currents.*—As the rings used in the experiments were not laminated, the question of the influence of the eddy currents set up in them on reversing the primary became an important one.

In J. J. Thomson's Recent Researches, the case of a cylinder placed in a uniform magnetic field which is suddenly destroyed

is considered, and it is shown how the total induction in the cylinder at any time  $t$  after the magnetic force is destroyed can be calculated if we know the value of  $\frac{4\pi\mu a^2}{\sigma}$ , where  $\mu$  and  $\sigma$  are the permeability and specific resistance of the material of the cylinder and  $a$  is its radius. We can make use of this result to form an approximate idea of the speed at which the secohmmeter might be driven without materially affecting the magnetic measurements.

The greatest permeability for alloy No. 1, which is the most permeable of the three specimens considered in this paper, was 680. If we take  $a$  as 0·6 cm. and  $\sigma$  as 20,000 (the temperature being 380° C.)  $\frac{4\pi\mu a^2}{\sigma} = 0\cdot15$ . A comparison with the table on p. 357 ('Recent Researches') will show that in this case the total induction will have diminished to 1 per cent. of its original amount in 0·1 of a second.

Hence we see that the number of alternations per second in the experiments on this alloy should be less than 10 per second, in order that the results may be relied upon to 1 per cent.

In general the secohmmeter made about 3 alternations per second. It could easily be seen whether, in any given case, the eddy currents were affecting the measurements, by obtaining a balance and then allowing the speed of the secohmmeter to increase.

The effect of eddy currents would be shown by the balance being disturbed.

Care was taken, during the experiments, that the speed of the secohmmeter should in all cases be less than that at which this occurred.

### § III. THE DETERMINATION OF THE TEMPERATURE.

The resistance of the secondary of the ring (which was of platinum wire and was wound next to the ring) was taken as a measure of the temperature. Thick platinum leads were connected to the secondary close to the ring, and after passing out of the box containing it dipped into mercury cups suspended in an oil-bath. From these cups copper wires passed to the key K<sub>4</sub> (fig. 3), by means of which the secondary could be connected at will to either the magnetic bridge or the wire bridge. Side by side with the platinum leads were placed compensating leads. These were cut from the same specimen of wire as that used for the leads to the secondary, and also dipped into mercury cups suspended in the oil-bath. Copper

wires of the same resistance as those connected to K<sub>4</sub> joined these cups with the key K<sub>3</sub>.

The object of the oil-bath was to maintain the junctions of platinum and copper at the same temperature, and thus get rid of thermoelectric currents.

The leads were protected from direct heating by the furnace by means of a thick sheet of asbestos.

The resistance-bridge H L M J was so arranged that the resistance of the secondary could be obtained directly from one observation.

This end was gained by the following device :—

The resistance of the arm HJ was made equal to 1001 ohms.

The resistance of MJ consisted of three parts, r<sub>2</sub>, r<sub>3</sub>, and ρ<sub>2</sub>.

r<sub>2</sub> was a resistance of 1000 ohms ; r<sub>3</sub> consisted of coils of tenths of an ohm ; and ρ<sub>2</sub> was part of the bridge-wire ηθ.

The resistance of the whole wire ηθ was slightly greater than 1 ohm. Hence, by taking the proper plugs out of r<sub>3</sub>, the resistance of ρ<sub>2</sub> and r<sub>3</sub> could be made together equal to one ohm to within one-twentieth of an ohm ; i.e., the resistance of the arm MJ is equal to 1001 ohms to within a twentieth of an ohm. To obtain a reading, the secondary and galvanometer are switched on to the wire-bridge by means of the keys K<sub>4</sub> and K<sub>2</sub>, and r<sub>4</sub> and ρ<sub>1</sub> are adjusted until there is a balance [with MJ=HJ].

When this is the case the resistance of the secondary is given by

$$r_t = r_4 + \rho_1.$$

The compensating leads are connected to the arm LM by the key K<sub>3</sub>.

The resistance of different lengths of the bridge-wire having been previously tabulated, the resistance of the secondary could be read off directly from the scale.

The temperature t of the ring of alloy was obtained from r, by means of Callendar and Griffiths's well-known formula

$$t = 100 \frac{r_t - r_0}{r_{100} - r_0} + \delta \left[ \left( \frac{t}{100} \right)^2 - \frac{t}{100} \right],$$

r<sub>100</sub>, r<sub>0</sub> being the values of r at 100° C. and 0° C. respectively, and δ having been obtained from observations in the vapour of boiling sulphur.

[To obtain the resistance of the secondary and leads together, the mercury cups 2 and 4 in the key K<sub>3</sub> were joined by a thick copper wire. Then we have, when balance has been obtained as before,

$$r_t + \text{leads} = r'_4 + \rho'_1.]$$

As the secondary is outside the ring whose temperature is required, care is necessary to insure that the temperature of the ring does not materially lag behind that of the thermometer.

To avoid the error due to this cause as far as possible, readings were only taken when the temperature was practically stationary.

The close agreement of the results obtained under different conditions shows that the temperature of the ring could not have been greatly different from that of the secondary. As it was impossible to read the magnetic bridge and the resistance bridge simultaneously, the time of each observation was recorded. A time and temperature curve was plotted, and from this the temperature at the time of taking a magnetic observation was inferred.

#### § IV. METHODS USED FOR VARYING THE TEMPERATURE AND FOR INSULATING THE COILS.

##### (1) *Experiments at High Temperatures.*

Asbestos paper was used as an insulator in these experiments. The specimen of paper used was obtained from Bell & Sons and was of a very superior quality. After heating to a white heat and subsequently cooling, the discolouration was very slight—the paper then having a faint yellow tinge. The paper also held well together after heating, and showed no signs of crumbling. The amount of carbonaceous matter present must have been very much less than that contained in the paper usually found in the market.

The paper was cut into strips of about 1 cm. width.

A double layer of this paper was wound next to the ring. Outside this the platinum secondary was wound, a double layer of paper being twisted round the wire during winding ; this thickness of paper being again doubled for the first and last wind. The primary was of copper wire insulated in the same way as the secondary, a double layer of paper being wound between the primary and secondary.

The ring when wound was placed in a copper box, to which a copper tube of about 8 inches in length was attached.

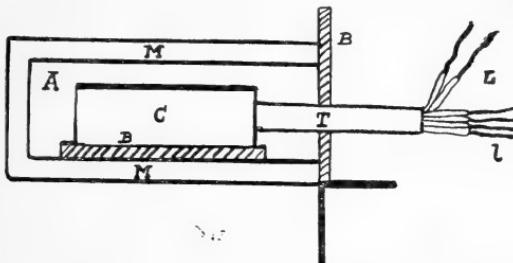
The box was placed in the muffle of a Fletcher's "Improved Muffle" Furnace, being separated from direct contact with it by means of a thick pad of asbestos board. The mouth of the muffle was closed with another piece of asbestos board, through a hole in which the tube attached to the box passed.

This copper tube, through which the leads passed, served

the double purpose of protecting them from the action of the furnace gases and at the same time of maintaining the temperature round them comparatively steady.

The arrangement of the apparatus is shown in fig. 5.

Fig. 5.



M = muffle.  
A = air-space.  
C = copper box.  
T = copper tube.

B, B = asbestos board.  
L = primary leads.  
l = secondary and compensating leads.

A small governor was connected up between the main gas-supply in the laboratory and the furnace. By this means the pressure of the gas at the furnace was kept constant.

The insulation-resistance between the primary and secondary was tested from time to time during the experiments. It was found to be always greater than 500,000 ohms.

## (2) Experiments at Temperatures between 0° C. and 50° C.

The ring was placed in a thin-walled copper box, which it almost completely filled. A piece of copper tubing of about one inch in length was fastened to one side of the box, and to this was attached a piece of glass tubing of about one foot in length, through which the leads passed. The glass tube was attached to the brass one by means of a joint made with Thomas's alloy. This alloy melts at about 75° C. and expands considerably on solidifying. If a piece of glass tubing is placed concentrically within a brass tube of somewhat greater diameter, and the melted alloy is run into the clear space between the two tubes, a very good mechanical air-tight joint is obtained. A glass tube is used to carry the leads in preference to a metal one, as it is desirable to prevent, as far as possible, the passage of heat between the cavity containing the ring and the external air.

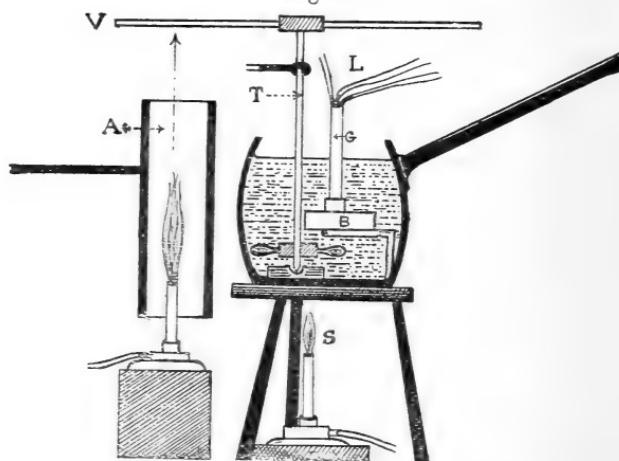
In working at temperatures much below zero this precaution was found very necessary.

The general arrangement of the apparatus is shown in

fig. 6. The box containing the ring was placed in a vessel of water which was heated from below by a bunsen-burner. The water was automatically kept in movement by means of a stirrer driven by a current of air passing through an asbestos cylinder and impinging upon a wind-wheel V.

To obtain temperatures between that of the atmosphere and that of ice, the source of heat was removed and small pieces of ice were added to the water from time to time until the desired temperature was obtained.

Fig. 6.



V = wind-wheel.

T = stirrer.

B = copper box.

G = glass tube.

L = leads.

S = source of heat.

A = asbestos cylinder.

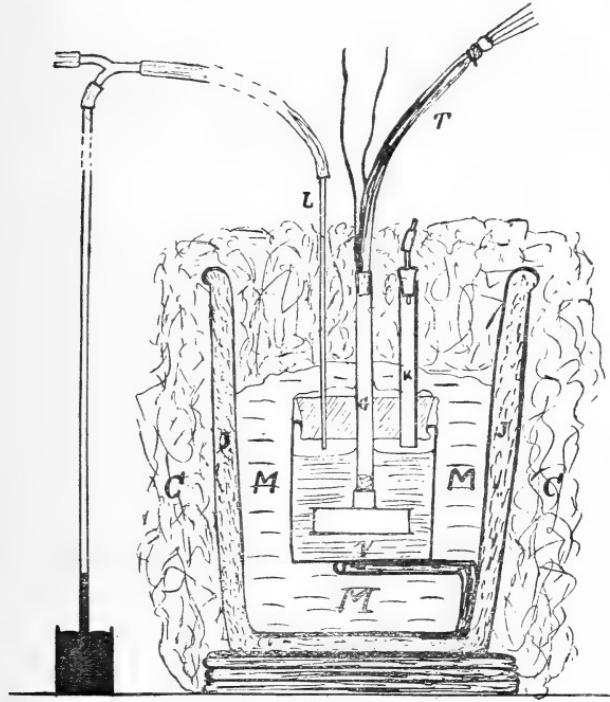
### (3) Experiments at Temperatures below Zero.

The same box and attached tube was used as in the last series of experiments. It was found that, at the low temperatures used, ice formed to the thickness of a centimetre or more along the metal leads, owing to the condensation of the moisture in the air, and thus the insulation was endangered.

To overcome this difficulty the following arrangement was adopted (fig. 7). The secondary and compensating leads were surrounded by an indiarubber tube T, the free end of which was carefully closed. Some portion of this tube passed down into the glass tube G. This was then filled with melted paraffin. By this means the access of moisture to the leads was confined to that in the indiarubber tube, and the formation of ice upon them was almost entirely stopped. The closing of the glass

tube also prevented the circulation of air between the surrounding atmosphere and the interior of the box, and the consequent heating of the ring. The box containing the ring was placed in the centre of a thin-walled metal vessel V, which was closed with a tightly-fitting bung through which the glass tube G passed. The vessel V was of about a pint and a half capacity, and was filled with ether, which was introduced through the tube K. The vessel was connected with a water-pump and manometer by means of another tube L. It was thus possible, by the rapid evaporation of the ether, to cool the

Fig. 7.



ring below the temperature of the surrounding medium, and by regulating the evaporation to vary the temperature at will. The bung was covered with melted paraffin before commencing an experiment, to insure air-tightness. The vessel V was placed in the cooling medium M contained in the large stone jar J, which rested on a thick pad of flannel. The whole arrangement was surrounded with a quantity of cotton-waste C. The cooling medium used in these experiments was either a mixture of ice and salt, or carbon-dioxide snow.

## § V. THE DATA OBTAINED, AND SOME REMARKS UPON THEM.

## Alloy No. I.

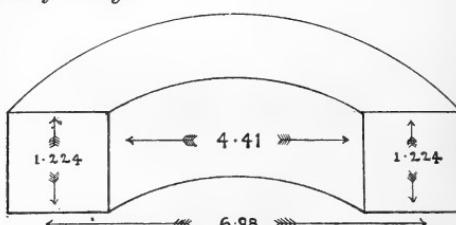
The first alloy investigated contained 3·64 per cent. of aluminium.

This alloy, in which the carbon was mostly in the form of graphite, was comparatively soft, and could easily be turned in a lathe. The other alloys, in which the carbon was mostly in the form of combined carbon, were harder than the hardest steel.

A complete analysis of this alloy, as supplied by Mr. Dawe, is as follows :—

Aluminium . . . . .	3·64 per cent.
Combined Carbon . . . . .	0·09 "
Graphite . . . . .	2·40 "
Silicon . . . . .	2·89 "
Sulphur . . . . .	0·007 "
Phosphorus . . . . .	1·086 "
Manganese . . . . .	0·301 "
Copper . . . . .	0·112 "
Chromium . . . . .	traces.
Iron (by difference) . .	89·47 per cent.
<hr/>	
	100·00

## Dimensions of Ring.



External diameter	=	6.98 cms.
Internal ,,"	=	4.41 ,,"
Mean ,,"	=	5.695 ,,"
Thickness ,,"	=	1.224 ,,"
Mean section	=	1.57 sq. cms.

## Other data.

Turns in Primary	=	87
Turns in Secondary	=	61
Mutual Inductance used in these experiments.	=	$1.155 \times 10^6$ .

The following readings of the induction were obtained for different temperatures, the maximum field reached at each reversal being maintained constant during any series of observations.

### In the tables

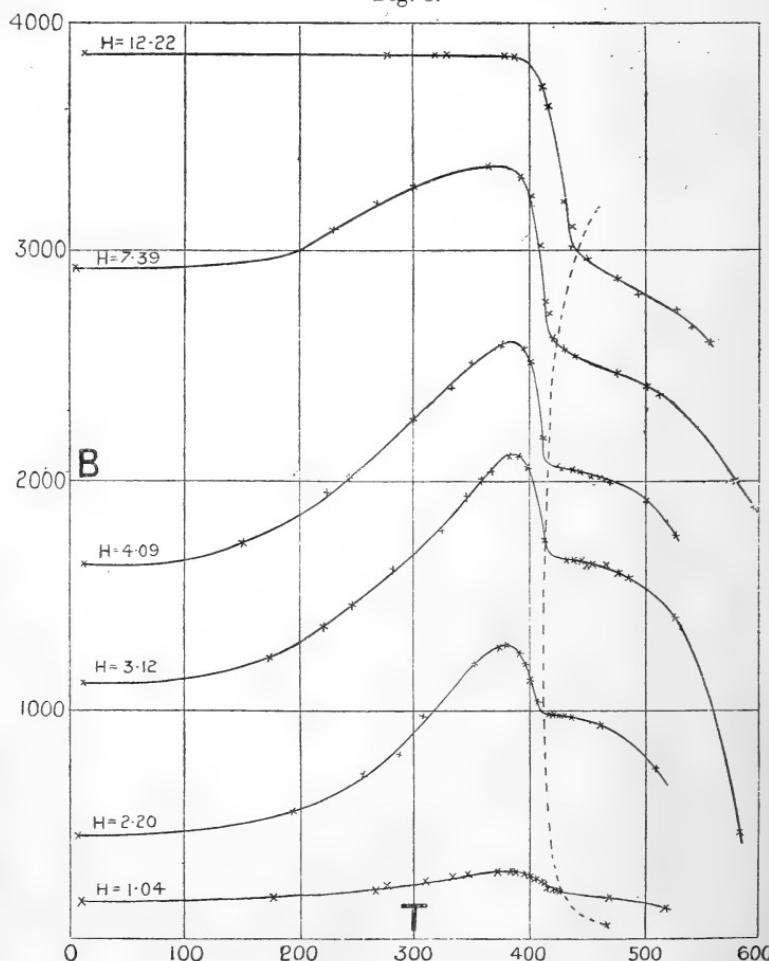
B stands for the induction, in C.G.S. units.

T " " temperature, in degrees centigrade.

H " " temperature, in degrees centigrade; field-strength, in C.G.S. units.

Curve (7).		$H = 0.49$ .		Curve (8).		$H = 1.96$ .	
T.	B.	T.	B.	T.	B.	T.	B.
14	67.7	400	91.0	15	367	585	219
172	75.9	426	81.5	305	736	624	67
230	83.3	434	73.1	345	895	693	18
247	86.3	443	67.2	435	714	785	3.4
300	92.7	462	61.0	457	714	888	3.4
315	96.0	469	59.1	483	681	943	3.4
365	101.0	516	50.8				
390	98.6	535	48.2				
		544	43.4				

Fig. 8.



These results are plotted on fig. 8 and on fig. 10. The curves obtained show that the maximum value of the induction

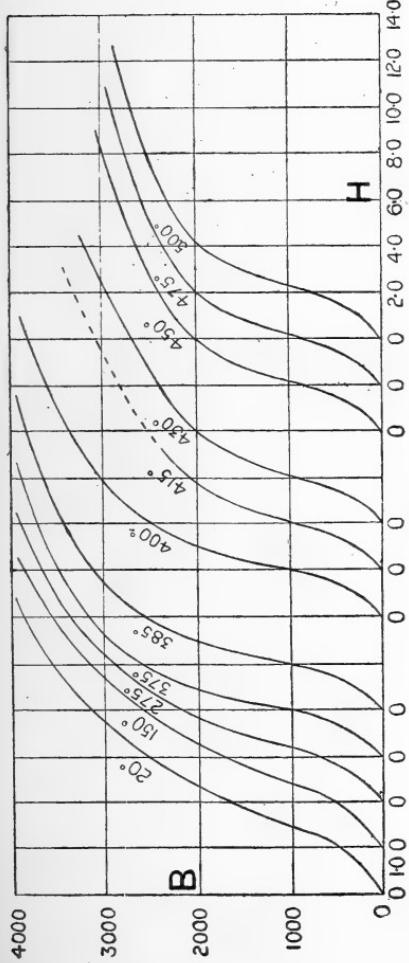
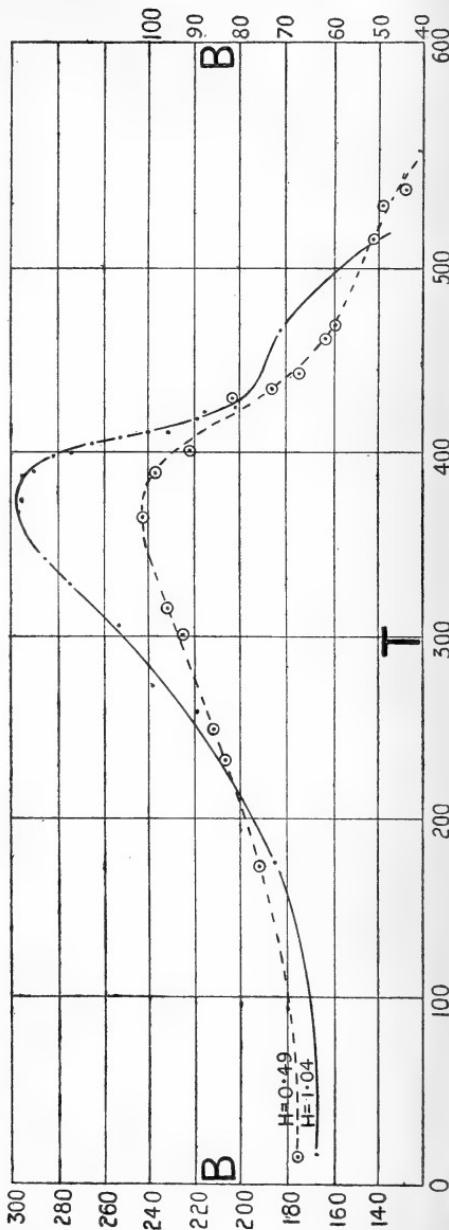


Fig. 9.

Fig. 10.



is reached at about  $380^{\circ}$  C. For the next  $40^{\circ}$  or so the curves are very steep, this steepness indicating a comparatively

sudden change in the permeability of the alloy. This steep part of the curve is followed by a very flat part extending over about  $100^{\circ}$ , for which range of temperature the permeability

Fig. 11.

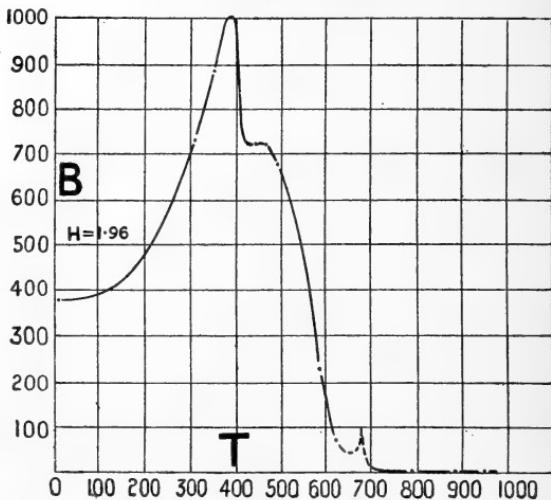
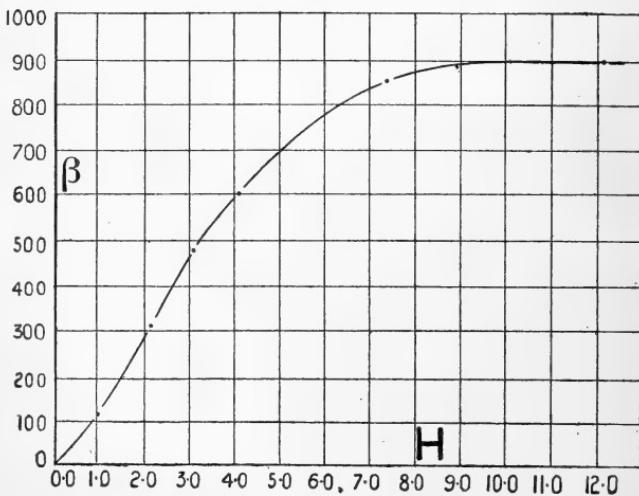


Fig. 12.



remains almost constant. This flat part is followed by a steep part extending to about  $600^{\circ}$ , when the curve begins to bend round again, finally becoming parallel to the axis of temperature at about  $750^{\circ}\text{C}$ .

This temperature was taken as the critical temperature for the ring of alloy.

At about  $660^{\circ}$  C. the curve develops a sharp point indicating an abrupt increase in the permeability followed by an equally abrupt decrease. This point will be discussed more fully in Part II.

It will be noticed that there are no sharp points in the curves at the temperatures of maximum and minimum permeability as might be expected to be the case if we were dealing with a substance of uniform consistency. This general roundness suggests that the alloy is heterogeneous in structure, the roundness being due to the different constituents reaching their maximum and minimum values at slightly different temperatures.

A complete curve, showing all the changes of induction with increasing temperature, is shown on fig. 11.

The relatively great steepness of the curve between the temperatures of  $385^{\circ}$  and  $420^{\circ}$  (about) is well shown in this figure.

This general form of curve was found to be common to all the alloys experimented on.

In all cases there is a very sudden change in the induction after passing the temperature of maximum induction, followed by a flatness extending in the case of the alloy containing 10 per cent. of aluminium over a considerable range of temperature, after which the curves again become steep.

It was thought that it would be interesting to ascertain whether the magnitude of this sudden change was in any way connected with the strength of the field.

To do this it is easy to select the temperature at which the induction is a maximum, as this is fairly well marked, and is about  $380^{\circ}$  C. The temperature at which the sudden change ceases does not, however, appear to be the same for all fields. The temperature  $450^{\circ}$  was arbitrarily chosen as that from which to measure the termination of the sudden change. The difference of B between these two temperatures is for shortness referred to as  $\beta$ .

The following values were obtained for  $\beta$  :—

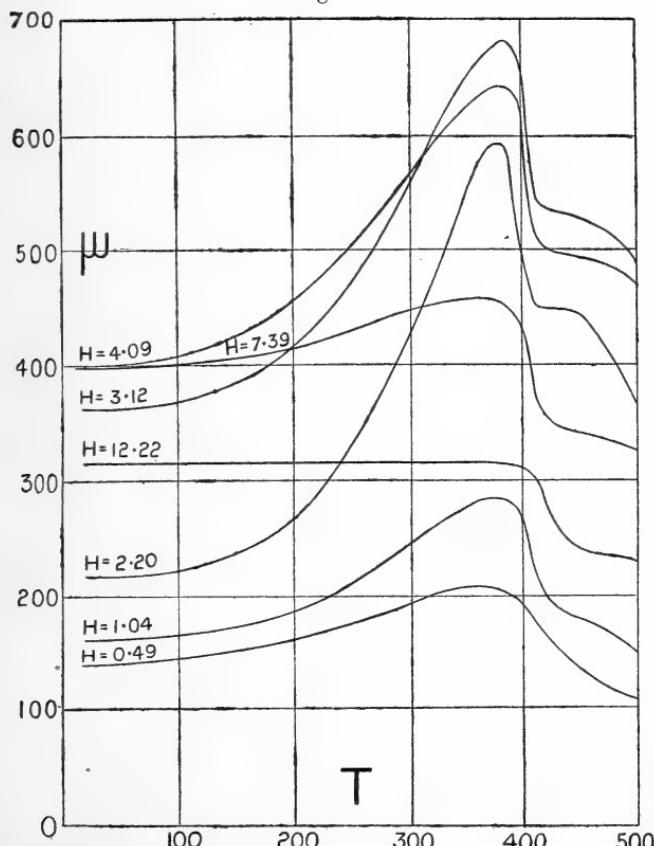
H.	B at $380^{\circ}$ .	B at $450^{\circ}$ .	$\beta$ .
12.22	3860	2960	900
7.39	3375	2520	855
4.09	2630	2030	600
3.12	2130	1650	480
2.20	1300	990	310
1.04	300	187	113

T=20° C.				T=415° C.			
H.	B.	H.	B.	H.	B.	H.	B.
12·22	3850	3·12	1120	12·22	(3630)	3·12	1680
7·39	2940	2·20	470	7·39	2700	2·20	990
4·09	1640	1·04	168	4·09	2080	1·04	225
T=150° C.				T=430° C.			
H.	B.	H.	B.	H.	B.	H.	B.
12·22	3850	3·12	1190	12·22	3200	3·12	1670
7·39	2970	2·20	510	7·39	2570	2·20	990
4·09	1740	1·04	178	4·09	2050	1·04	197
T=275° C.				T=450° C.			
H.	B.	H.	B.	H.	B.	H.	B.
12·22	3850	3·12	1580	12·22	2960	3·12	1650
7·39	3230	2·20	810	7·39	2530	2·20	980
4·09	2170	1·04	235	4·09	2030	1·04	187
T=375° C.				T=475° C.			
H.	B.	H.	B.	H.	B.	H.	B.
12·22	3855	3·12	2110	12·22	2870	3·12	1610
7·39	3380	2·20	1300	7·39	2480	2·20	910
4·09	2620	1·04	298	4·09	2000	1·04	176
T=385° C.				T=500° C.			
H.	B.	H.	B.	H.	B.	H.	B.
12·22	3850	3·12	2130	12·22	2820	3·12	1530
7·39	3360	2·20	1300	7·39	2420	2·20	810
4·09	2630	1·04	296	4·09	1940	1·04	156
T=400° C.							
H.	B.	H.	B.				
12·22	3820	3·12	2040				
7·39	3250	2·20	1110				
4·09	2520	1·04	278				

These results are plotted on fig. 12. The curve obtained is very similar in general shape to a B and H curve, and does not differ materially in shape from the analogous curves for the next alloy considered. The changes of the induction with temperature are, in fact, of the same nature as those we should obtain if we were dealing with two rings of different compositions superposed one upon the other.

The B and H curves shown on fig. 9 were obtained from the readings given in the Table on p. 140.

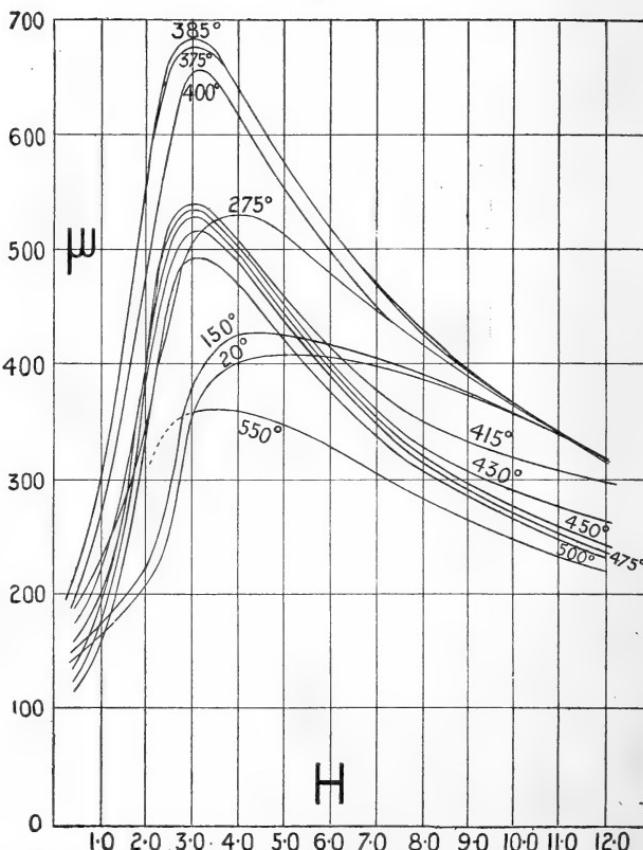
Fig. 13.



On figs 13 & 14 are shown the curves connecting (1) the permeability and temperature when the maximum field reached at each reversal is maintained constant, and (2) the permeability and field-strength when the temperature is constant. The greatest permeability is reached at  $380^\circ\text{C}$ . for fields of about 3.0 C.G.S. units, but the increase in per-

meability between  $20^\circ$  and  $380^\circ$  is greatest for fields of about 2.2 C.G.S. units. The curves are more rounded in general outline both for high and low fields than for fields of medium strength.

Fig. 14.



The values from which these curves were obtained are given below (Table opposite page).

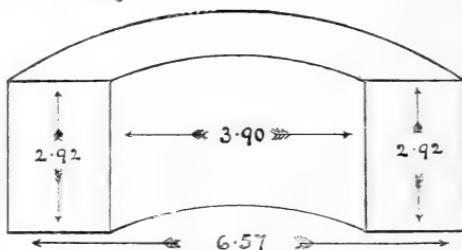
#### *Alloy No. II.*

This alloy contained about 10 per cent. of aluminium. It was too hard to be cut by ordinary tools. The molten metal was cast into a ring of 6.57 cms. external diameter, and 2.92 cms. thick. The ring was subsequently cut into two by means of a diamond wheel, and an analysis was made of the upper half.

T.	H.	$\mu.$	T.	H.	$\mu.$
20°	12·22	315	150°	12·22	315
	7·39	398		7·39	402
	4·09	401		4·09	425
	3·12	359		3·12	382
	2·20	214		2·20	232
	1·04	161·5		1·04	171
	0·49	139		0·49	151
275°	12·22	315	375°	12·22	316
	7·39	437		7·39	457
	4·09	530		4·09	640
	3·12	507		3·12	675
	2·20	368		2·20	591
	1·04	226		1·04	286
	0·49	184		0·49	206
385°	12·22	315	400°	12·22	313
	7·39	454		7·39	439
	4·09	643		4·09	616
	3·12	683		3·12	654
	2·20	591		2·20	505
	1·04	285		1·04	267
	0·49	204		0·49	192
415°	12·22	297	430°	12·22	262
	7·39	366		7·39	348
	4·09	508		4·09	501
	3·12	539		3·12	535
	2·20	450		2·20	450
	1·04	216		1·04	189
	0·49	173·5		0·49	155
450°	12·22	242	475°	12·22	235
	7·39	342		7·39	336
	4·09	496		4·09	489
	3·12	529		3·12	516
	2·20	446		2·20	414
	1·04	180		1·04	169
	0·49	135		0·49	118
500°	12·22	231	550°	12·22	217
	7·39	327		7·39	298
	4·09	474		3·12	359
	3·12	491			
	2·20	368			
	1·04	150			
	0·49	110			

*Analysis of upper half (by Mr. Dawe).*

Aluminium . . . . .	9.89
Combined Carbon . . . . .	2.80
Graphite . . . . .	traces
Silicon . . . . .	2.75
Sulphur . . . . .	traces
Phosphorus . . . . .	0.57
Manganese . . . . .	trace
Copper . . . . .	nil
Chromium . . . . .	nil
Arsenic . . . . .	nil
Iron (by difference) . . . . .	83.99
	100.00

*Dimensions of Ring.*

External diameter . . . . .	6.57 cms.
Internal " . . . . .	3.90 "
Mean " . . . . .	5.23 "
Mean thickness . . . . .	2.92 "
Mean section . . . . .	3.88 sq. cms.

*Other data.*

Turns in Primary . . . . .	63
Turns in Secondary . . . . .	36
Standard Mutual Inductance used	$= 1.155 \times 10^6$ .

The curves connecting B and T ( $H = \text{const.}$ ) for this alloy are shown on figs. 15 and 16.

A study of these curves in conjunction with the corresponding ones for the Alloy No. I leads to the conclusion that the maximum value of the induction is probably reached at a temperature of about  $-90^\circ \text{C}$ . The great change in the induction between this temperature and  $+100^\circ \text{C}$ . is very striking, the value at  $100^\circ$  being about one-quarter of that at  $-90^\circ \text{C}$ . and about one-half of that at  $20^\circ \text{C}$ .

The curves show for weak fields a second maximum between  $300^\circ$  and  $400^\circ$ , after which the induction falls off to a minimum value at about  $460^\circ$  when the permeability  $\doteq 1.7$ . All the methods for varying the temperature (*vide* § IV.) were called into requisition in the experiments on this alloy. The method used in obtaining each series of observations is indicated above the series in the tables given below.

Fig. 5.

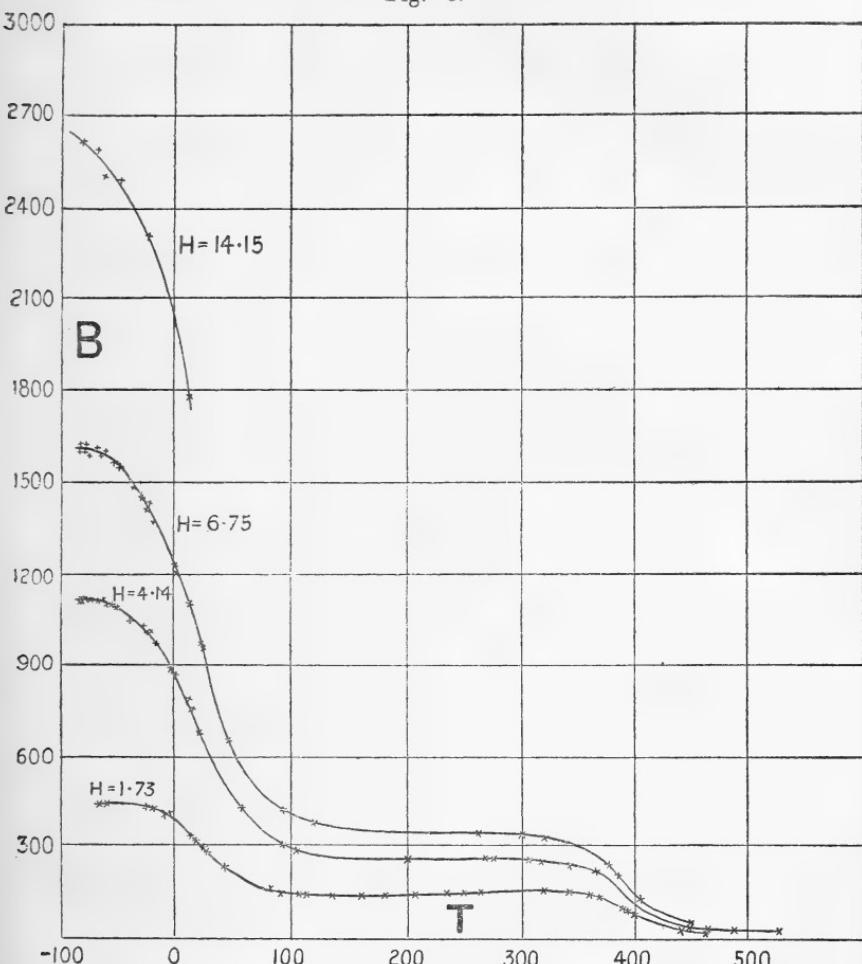
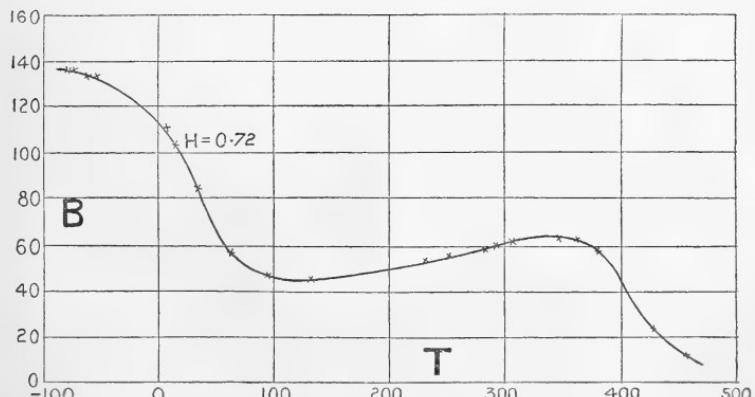


Fig. 16.



## Data obtained from Experiments at High Temperatures

H.	T.	B.	H.	T.	B.
6·75	12	1099	6·75	321	303
	22	951		377	232
	45	641		385	192
	93	404		404	113
	120	359		448	33·4
	263	328		486	12·9
	300	314			
4·14	14	745	4·14	309	238
	57	419		320	232
	90	300		342	219
	104	276		366	206
	200	254		448	24·3
	270	250		461	14·6
	277	245		525	7·0
1·73	13	313	1·73	88	133
	22	282		106	128
	40	223		112	128
	80	148		250	136
	132	125		359	127
	160	126		367	122
	181	127		389	89·5
	207	131		392	74·6
	236	135		398	64·5
	263	136		439	13·5
	320	137		460	5·5
	341	135			
0·72	14	105	0·72	292	59·0
	34	85·5		307	60·4
	62	55·3		343	61·8
	93	45·0		362	61·3
	131	45·2		379	57·7
	230	52·3		427	23·7
	250	55·0		454	10·1
	281	57·7			

Data from Experiments in Ether Bath surrounded by a mixture of ice and salt.

H.	T.	B.	H.	T.	B.
6·75	- 2	1242	4·14	- 6	880
	- 20	1370		- 20	966
	- 26	1405		- 26	1000
1·73	-10	393			
	-20	420			
	-25	425			

Data from Experiments in Ether Bath surrounded with  
 $\text{CO}_2$  snow (First Series).

H.	T.	B.	H.	T.	D.
14·15	-80	2620	14·15	-48	2485
	-68	2590		-22	2260
	-61	2500		+13	1775
6·75	-81	1612	6·75	-61	1587
	-80	1612		-51	1550
	-77	1603		-28	1422
	-68	1600		+11	1103
4·14	-82	1106	4·14	-62	1094
	-80	1106		-53	1082
	-78	1117		-24	1002
	-69	1102		+11	775
1·73	-69	434	1·73	+10	321
0·72	-79	137	0·72	-62	133
	-79	137		-54	133
	-77	137		+ 9	111

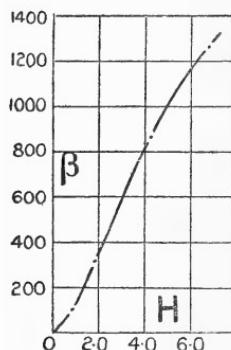
Data obtained from Experiments in Ether Bath surrounded by  $\text{CO}_2$  snow (Second Series).

H.	T.	B.	H.	T.	B.
6·75	-83	1595	6·75	-38	1477
	-80	1595		-29	1443
	-75	1587		- 1	1207
	-66	1580		+20	960
	-55	1560			
4·14	-80	1110	4·14	-42	1040
	-76	1110		-29	1020
	-67	1105		- 3	860
	-56	1090		+20	673
1·73	-65	434	1·73	- 6	393
				+20	294

$\beta$  for this alloy represents the difference in the values of the induction at (1)  $-90^\circ \text{C}$ , and at (2) the temperature of the lowest point reached by the B and T curves between  $100^\circ$

and  $200^{\circ}$  C. The results are given below, and the curve obtained from them is shown on fig. 17.

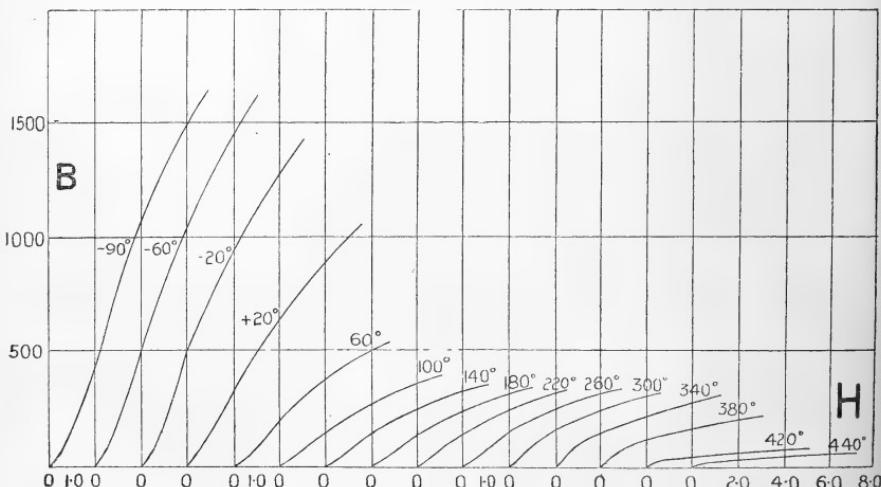
Fig. 17.



The curve obtained is similar in general form to a B and H curve.

H.	$\beta$ .
6.75	(1600 - 340)
4.14	(1110 - 250)
1.73	( 435 - 130)
0.72	( 138 - 44)
	1260
	860
	305
	94

Fig. 18.



The B and H curves at constant temperature, shown on fig. 18, were obtained from the following readings :—

T = -90° C.		T = -60° C.	
H.	B.	H.	B.
6.75	1605	6.75	1583
4.14	1110	4.14	1095
1.73		1.73	435
0.72	138	0.72	134
T = -20° C.		T = +20° C.	
6.75	1385	6.75	990
4.14	968	4.14	675
1.73	420	1.73	285
0.72	123	0.72	100
T = 60° C.		T = 100° C.	
6.75	533	6.75	390
4.14	400	4.14	280
1.73	175	1.73	130
0.72	57	0.72	45
T = 140° C.		T = 180° C.	
6.75	350	6.75	338
4.14	255	4.14	248
1.73	125	1.73	125
0.72	45	0.72	47.5
T = 220° C.		T = 260° C.	
6.75	335	6.75	330
4.14	255	4.14	250
1.73	130	1.73	135
0.72	50.5	0.72	55.5
T = 300° C.		T = 340° C.	
6.75	320	6.75	295
4.14	245	4.14	225
1.73	140	1.73	135
0.72	60.5	0.72	63

T=380° C.		T=420° C.		T=440° C.	
H.	B.	H.	B.	H.	B.
6.75	218	6.75	68	6.75	45
4.14	160	4.14	50	4.14	30
1.73	105	1.73	30	1.73	15
0.72	57	0.72	28	0.72	14

*Alloy No. III.*

The third alloy investigated contained 18.47 per cent. of aluminium. It was exceedingly hard. The molten metal was cast into a disk, and a hole was bored through the central part of this by means of the emery cylinder. The critical temperature was found to be about 25° C.

The experiments give no evidence of temperature hysteresis—the B and T curves obtained with rising temperatures being identical with those obtained with falling temperatures.

The great similarity between these curves and the latter part of those for Alloy No. II. (*e.g.* the part above 200° C.) leads to the conclusion that the maximum value of the induction is probably attained at a temperature much below any reached in the experiments.

The curves on fig. 19 (p. 153) show that the values of the induction obtained in the experiments on this alloy can, in the main, be relied on to  $\frac{1}{10}$  of a line.

The largest induction observed during the experiments was about 21.5 lines, and the smallest about 2.4 lines.

The greatest permeability was equal to 3.7.

As in the case of the other alloys, there is a remanent permeability after the critical temperature is passed; its value is about 1.5. A curve connecting the temperature and time during cooling did not indicate an evolution of heat on passing the critical point.

As, however, the cooling took place in the air, the test is not sensitive, and this result cannot be regarded as of much value.

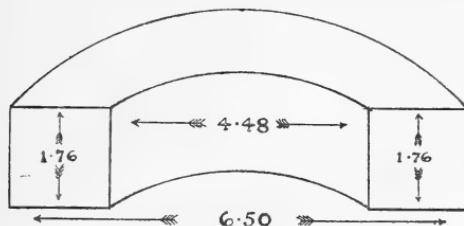
The temperature of the alloy during the experiments was regulated by the methods 2 and 3 described in § IV.

*Dimensions of Ring.*

External diameter . . . . .	6.50	cms.
Internal      "      . . . . .	4.48	"
"      thickness . . . . .	1.76	"
Mean Section . . . . .	1.78	sq. cms.

## Other data.

Turns in Primary . . . . . 82  
 Turns in Secondary . . . . . 37  
 Standard Mutual Inductance used =  $4.536 \times 10^5$ .



## Analysis (by Mr. Dawe).

Aluminium . . . . .	18.47	per cent.
Combined Carbon . . . . .	1.56	"
Graphite . . . . .	0.10	"
Silicon . . . . .	1.47	"
Phosphorus . . . . .	0.651	"
Manganese . . . . .	0.25	"
Chromium . . . . .	0.00	"
Copper . . . . .	traces	
Iron (by difference) . . .	77.50	"

## I.—Experiments with Rising Temperature.

H.	T.	B.	H.	T.	B.
6.11	6	13.1	1.63	7.0	3.6
	8	12.5		8.5	3.4
	20	10.0		19.5	2.7
	37	9.1		37.5	2.5
	51.5	8.6		51.5	2.4
	43 (Temp. falling)	9.0		43 (Temp. falling)	2.4
3.56	6.5	7.6			
	8.5	7.3			
	19.5	5.8			
	37.5	5.4			
	51.5	5.2			
	43 (Temp. falling)	5.4			

## II.—Experiments with Falling Temperatures.

H.	T.	B.	H.	T.	B.
6.11	43	9.0	1.63	42	2.4
	26	9.5		26	2.5
	10	11.8		10	3.2
3.56	43	5.4			
	26	5.4			
	10	6.9			

III.—Experiments in Ether Bath, surrounded by CO<sub>2</sub> snow.

H.	T.	B.	H.	T.	B.
6.11	-83	21.0	1.63	-83	5.5
	-80	20.9		-80	5.5
	-78	20.9		-79	5.5
	-74	21.0		-74	5.4
	-63	21.2		-64	5.5
	-50	21.5		-54	5.5
	-31	21.4		-35	5.5
	-14	19.0		-15	5.0
	+1	15.2		0	3.9
	21°.1	9.6		21°.1	2.6
3.56	-83	12.1			
	-80	12.0			
	-78	12.1			
	-74	12.0			
	-63	12.2			
	-53	12.4			
	-33	12.3			
	-14	10.9			
	+1	8.8			
	21°.1	5.6			

These results are plotted as fig. 19.

The B and H curves shown as fig. 20 were obtained from the following readings:—

H.	B. T = -80°.	B. T = -40°.	B. T = 0°.	B. T = 40°.	B. T = 50°.
6.11	21.0	21.6	15.5	9.0	8.7
3.56	12.0	12.0	8.8	5.4	5.4
1.63	5.5	5.5	4.0	2.4	2.4

It is not proposed at this stage to enter at length into a consideration of the explanation of the observed phenomena; but it is interesting to notice that the characteristic B and T

Fig. 19.

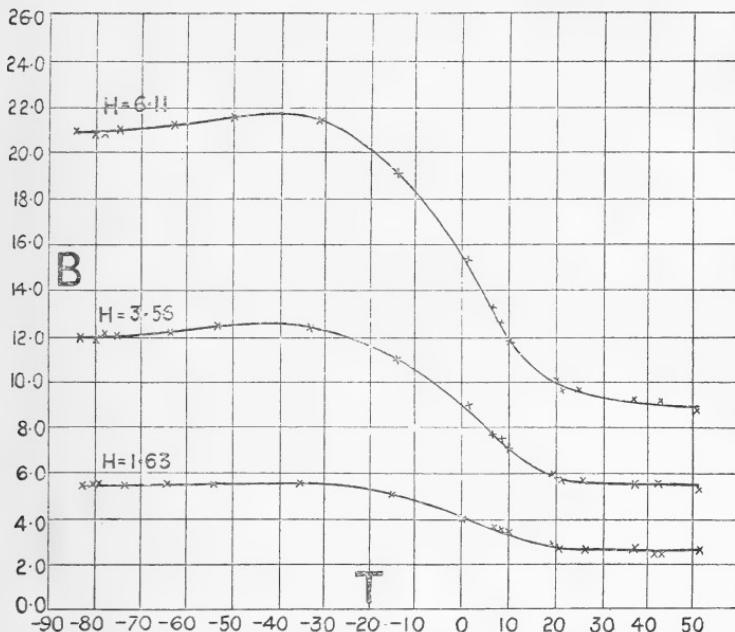
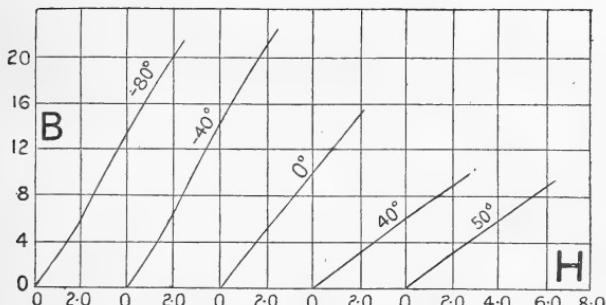


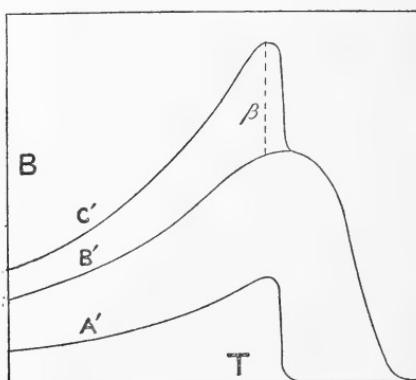
Fig. 20.



curve is of the same form as that which would be given by the superposition of two media of different constitution, as for instance crystals in a solidified mother-liquid. That this is so can easily be seen by the consideration of the following diagram.

Suppose, for instance,  $A'$ ,  $B'$  are the curves obtained by plotting the parts of the induction contributed by each medium independently against the temperature for any given value of  $H$ ; then the curve  $C'$  obtained by adding the ordinates will represent the observed  $B$  and  $T$  curve for the alloy in question.

Fig. 21.



The value of  $\beta$  for this curve, which approximates to the maximum value of the ordinate of the curve  $A'$ , would then be connected with  $H$  by a curve similar to a  $B$  and  $H$  curve.

This result is in agreement with the curves actually obtained from the experiments.

It is intended very shortly to publish an account of some further experiments on the changes of hysteresis as the temperature rises, and on the behaviour of the alloys during cooling.

In conclusion, the author's best thanks are due to Mr. Dawe, F.I.C., Chemist to the Ebbw Vale Ironworks, for his kindness in making the very complete analyses of the alloys, and to Prof. J. J. Thomson for suggestions and encouragement during the progress of the work.

University College, Nottingham.

IX. *Proceedings of Learned Societies.*

## GEOLOGICAL SOCIETY.

[Continued from vol. xlvi. p. 572.]

November 22nd, 1899.—W. Whitaker, B.A., F.R.S., President,  
in the Chair.

THE following communications were read:—

1. 'On some Remarkable Calcisponges from the Eocene Tertiary Strata of Victoria (Australia).' By George Jennings Hinde, Ph.D., F.R.S., F.G.S.

2. 'The Silurian Sequence of Rhayader.' By Herbert Lapworth, Esq., F.G.S.

This paper opens with a general reference to the Ordovician and Silurian complex of Central Wales, and a notice of the geological work hitherto done in the region. The stratigraphical relations of the Silurian formations which occur in the country surrounding the town of Rhayader (Radnorshire) are then described in detail. Typical and confirmatory sections are given, demonstrating the complete local sequence of the rocks of the Rhayader district. These are illustrated by lists of characteristic graptolites. These fossils are compared with those of Southern Scotland, Sweden, and North Wales, showing that the graptolite-succession is everywhere similar, and fixing the age of the Rhayader Series as representing the Lower Llandovery, Upper Llandovery, and Tarannon of other areas. Finally, several new species of *Climacograptus* and *Diplograptus* are described.

The author establishes the following sequence:—

## Rhayader Group (Pale Shales).

=Gala and Tarannon Group.

Caban Group.	Gafallt Beds.	<i>Gafallt Shales.</i> <i>M. Sedgwicki-grits.</i>	}=Upper Llandovery, May Hill, and Upper Birkhill.
	Caban Con- glomerates.	<i>Upper Conglomerate.</i> <i>Intermediate Shales.</i> <i>Lower Conglomerate.</i>	

Gwastaden Group.	Gigrin Mudstones.	<i>Pale Grey Mudstones.</i> Zone of <i>M. convolutus</i> . Calcareous Nodule-beds.	}=Lower Llandovery and Lower Birkhill.
	Ddôl Shales.	Zone of <i>M. fimbriatus</i> . ,, <i>M. cyphus</i> . ,, <i>M. tenuis</i> .	
	Dyffryn Flags.	<i>D. modestus</i> -flags. Rottenstone Beds. Micaceous Flags & Grits.	
	Cerig Gwynion Grits.		

Blue-black Shales.

=Bala and Hartfell.

No single section, taken in any direction across the Rhayader

country, shows the complete succession. In any area some one group is always better developed than others; and some portion of at least one group is certain to be missing. The lowest, or Gwastaden Group, has a maximum thickness of over 1800 feet. It is underlain, apparently conformably, by highly-cleaved dark blue shales, and overlain unconformably by both the Caban and Rhayader Groups. The base of the Gwastaden Group is formed of a thick mass of grauwackes, which thin to the east and thicken to the west. They contain *Climacograptus*, and pass up into mixed flags and grits with *Climacograptus* and *Diplograptus*. These are succeeded by shales and mudstones in which the first Monograptidæ appear. These become dominant in the upper part.

The succeeding Caban Group has a maximum thickness of 1500 feet. Its lower division consists of two massive conglomerates, separated by shales; its higher division is made up of fine-grained grits, shales, and flags. Each member of the group is overlapped to the east by the next sub-group above it, until eventually the whole group disappears beneath the Rhayader Pale Shales, which in the eastern areas rest directly on the Gwastaden rocks.

The Rhayader Group consists of pale green, blue, and grey shales and mudstones, which overstep on to the Gwastaden beds; and may possibly pass completely over them, and rest on the dark shales farther east.

After the Gwastaden rocks were laid down, the sea-floor appears to have been elevated and denuded, a hollow being scoured out to the eastward. Rapid sinking followed; and the sea filled the hollow with the Caban sediments, practically levelling it up by the time that the deposition of the Pale Slates began.

Tables of fossils enable the author to establish a complete comparison of the whole of the local zones of the Rhayader district with those of Southern Scotland, Wales, and Sweden. In the Rhayader area we find, for the first time in Britain, the entire Valentian succession developed in one general sequence of rocks, with a more or less common lithological character and with a fauna composed throughout of similar palæontological types.

December 6th.—W. Whitaker, B.A., F.R.S., President,  
in the Chair.

Dr. BLANFORD said that he had been asked by Prof. JUDD, who was unable to attend, to say a few words about certain photographs sent by Mr. E. H. L. Schwarz, and representing the Dwyka boulder-bed and the rounded and grooved underlying surface, in the neighbourhood of the Orange River near Hopetown and Prieska. The importance of these photographs lay in the evidence which they afforded on a disputed point. Dr. Sutherland and Mr. Griesbach had called attention to the evidence of ice-action presented by the Dwyka Conglomerate in Natal, and additional evidence had been brought forward by several observers, especially by Mr. Dunn from the Orange

Free State and Cape Colony, and recently by Dr. Molengraaff from the Transvaal. Other observers however, and especially the late Prof. Green, had disputed the glacial origin of the Dwyka beds. The photographs now exhibited would, the speaker thought, convince most geologists that the phenomena presented were due to ice-action. The resemblance to similar photographs shown to the Society in 1896 by Prof. T. W. Edgeworth David, and representing the beds corresponding to the Dwyka Conglomerate in South Australia, was noteworthy. Evidence of glacial action in Upper Palæozoic times had gradually accumulated from India, Australia, and South Africa, and there was a probability that similar indications existed in South America.

The following communications were read:—

1. 'On the Geology and Fossil Corals and Echinids of Somaliland.' By Dr. J. W. Gregory, F.G.S.

British Somaliland consists of a high plateau, of which the northern scarp is separated from the Gulf of Aden by a belt of low hills and plains known as the Cuban. The southern plateau consists of Archæan gneisses, quartzites, amphibolite-schists, chloritic schists, and pegmatites. It is capped by purple grits, red sandstones, and conglomerates, which are covered by limestones of Neocomian, Turonian (?Cenomanian), and Eocene ages. The Neocomian limestone, which may be correlated with that of Singeli described by Rochebrune, occurs at Dobar in the Cuban; while a Jurassic limestone, probably of Bathonian date, occurs at Bihendula in the Cuban. Fossils collected from these limestones and from raised reefs of Pleistocene age, by Mr. and Mrs. Lort Phillips, Miss Gillet, Mr. G. P. V. Aylmer, Capt. E. T. Marshall, and Mr. F. B. Parkinson, have been examined by the author, who tabulates a list of corals and echinids. One new genus and fourteen new species of corals are described, belonging to the genera *Stylophora*, *Styliina*, *Columnastræa*, *Prionastræa*, *Favia*, *Metethmos*, *Cyclolites*, and *Lithastræa*, and one new species of *Pseudodiadema*. The evidence of the collections is sufficient to show that a Neocomian limestone occurs both on the summit of the Somali plateau and on the floor of the Cuban, and that some marine limestones of Lower Tertiary age (probably Eocene) also occur on the plateau. It is therefore evident that the foundering of the Aden Gulf is post-Eocene in age.

2. 'Note on Drift-gravels at West Wickham (Kent).' By George Clinch, Esq., F.G.S.

The author describes two beds of Drift-gravel at West Wickham. The first, occupying the bottom of a dry valley, yields, in a section exposed at Gates Green, material derived from the Chalk and the Lower Greensand; and distinct, although perhaps not direct, relation with the denudation of the Weald is claimed for it. The other bed of gravel is of later age, and has yielded many Palæolithic imple-

ments and flakes. The specimens of these exhibited were found by the author between 1880 and 1885, and they establish the existence of Drift-gravels about a mile south of Hayes Common. Some of the implements have lost their pointed ends and bear other indications of use, many are smoothed and rounded by Drift-wear, but a few are entirely unworn, while some, particularly the larger examples, are bruised and crushed by such influences as the plough-share and wagon-wheels. Most of the implements have a superficial colouring, varying from a pale straw-tint to a rich ochreous-brown. ‘The association of much-worn implements, unworn implements, and flakes, cores, and waste-chips, in the same bed of Drift-gravel points to the fact that we have here a collection of material which was brought from a great variety of places, and has undergone a great variety of conditions and changes.’

3. ‘On the Occurrence in British Carboniferous Rocks of the Devonian Genus *Palaeoneilo*, with a Description of a New Species.’ By Dr. Wheelton Hind, B.S., F.R.C.S., F.G.S.

## X. *Intelligence and Miscellaneous Articles.*

ON KERR’S PHENOMENON. BY MM. ABRAHAM AND LEMOINE.

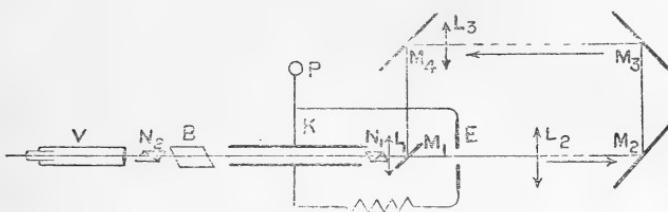
**L**IQUID dielectrics, sulphide of carbon for example, become birefringent when placed between the armatures of a condenser. The liquid is equivalent to a crystal whose axis is normal to the faces of the condenser. It is shown by passing between the plates a luminous beam polarized at  $45^\circ$  to the axis. A nicol analyser cannot extinguish it.

When the electric field is done away with the birefringence dies out during an inappreciable space of time. M. Blondlot has shown, by a method founded on the use of a revolving mirror, that the optical phenomenon does not exist more than  $\frac{1}{40,000}$  second after the removal of the electric field. The authors have been able to shorten this interval.

The condenser K is charged by connecting it with the poles P of a high-voltage transformer. It is discharged suddenly in the spark E, which is divided by an air-blast. If the amount of birefringence during this discharge is measured, it should show that this birefringence disappears during a very short time. MM. Abraham and Lemoine have proved that it diminishes to half in  $\frac{1}{400,000,000}$  second, and that it is no longer measurable in a little over  $\frac{1}{100,000,000}$  second.

The measurement of the birefringence is made by employing the discharge-spark E as source of light; it is very luminous and of very short duration. The elliptic light which comes from the condenser K is analysed by the so-called photometric method; it traverses the double-image prism B and an analysing nicol N<sub>2</sub>. The

principal section of the double-image prism is parallel to that of the polarizing nicol  $N_2$ . The two images furnished by this system are



observed by means of a telescope V. By a suitable rotation of the Nicol  $N_2$ , these two images can be brought to the same intensity; this rotation of the Nicol measures the difference of mean phase due to Kerr's phenomenon during the passage of the luminous flow in the condenser.

A continuous source of light (sun, electric arc, &c.) cannot be employed; the spark presents the advantage of being produced only at the moment of the discharge and of having a duration comparable to that of the disappearance of the birefringence. The experiment furnishes therefore, together with the result sought for, the evaluation of the order of the length of duration of the spark.

The light of the spark is brought into the condenser, at different periods, by the following arrangement:—The converging lens  $L_1$  renders the luminous beam cylindrical to enable it to traverse the interval between the plates of the condenser (mirror  $M_1$  removed). On the other hand, putting the mirror  $M_1$  in place, the system of two converging lenses,  $L_2$ ,  $L_3$ , and four plane mirrors  $M_2$ ,  $M_3$ ,  $M_4$ ,  $M_5$  will bring the light of the spark to the condenser.

By displacing the two mirrors  $M_2$ ,  $M_3$  the length of path  $EM_2M_3M_4M_5$  which the light of the spark traverses before arriving at the condenser K can be varied.

The first measurement, made with the mirror  $M_1$  removed, gives the value of the phenomenon at the instant when the spark E appears, or, at the latest, at the end of the time which light takes to traverse the path EK, which is about 20 centimetres.

In the following measurements,  $M_1$  being in place, the time which elapses between the production of the spark and the instant when the light passes K can be increased at will; it is only necessary to draw back by degrees the mirrors  $M_2$ ,  $M_3$ . In this manner one can, after a fashion, construct the curve of the phenomenon as a function of the time, a delay of one metre corresponding to one three-hundred-millionth of a second.

The results of one experiment are as follows:—

Path traversed. cm.	Rotation of the Nicol. °
20	17.3
100	8.7
400 and over.	not measurable.

These measurements establish the result predicted. Between the first experiment and the second the light traversed 0·80 metre in a time equal to  $\frac{0\cdot80}{300,000,000}$  or about  $\frac{1}{400,000,000}$  of a second, and the phenomenon diminished from 17°·3 to 8°·7, that is to say by one half. After  $\frac{4}{300,000,000}$  of a second the phenomenon was no longer appreciable.

MM. Abraham and Lemoine also exhibited to the Society an arrangement which enables the birefringence of conductors to be shown. The water which fills the tank of Kerr's condenser is operated on. The condenser is placed between two crossed nicols suitably situated. The spark E is always the source of light employed.

The manner of charging the condenser is different. The poles of the transformer charge two condensers by cascade; the exterior armatures of these condensers are connected by a resistance of which the condenser K forms part. During the charge the water plays the part of a conductor. At the moment when the spark passes, the charges suddenly set free on the auxiliary condensers proceed to charge the condenser K, and during this sudden action the water acts as an insulator. The Kerr's condenser keeps its charge for a very short time, and a brilliant reappearance of light is observed.—*Séances de la Société Française de Physique*, Nov. 17, 1899.

OBITUARY NOTICE : DR. J. L. HOWARD.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,

Will you allow me to make use of your pages to announce the death of Dr. J. L. Howard, at the age of 33, after an exceptionally strenuous life.

His initials were frequently appended to translations and reviews in your columns. He published a joint paper with me (July 1889) on the Refraction of Hertz Waves by Pitch Lenses. He was first a student and then a Demonstrator for 12 years at University College, Liverpool; and between the two stages he had studied under Professor Quincke at Heidelberg, and contributed a paper in conjunction with Dr. Lenard to Wiedemann's *Annalen* on the Change of Resistance of Bismuth in a Magnetic Field.

As an industrious and learned physicist his early death is deeply to be deplored.

I am, Gentlemen,  
Your obedient servant,  
OLIVER J. LODGE.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

FEbruary 1900.

XI. Radioactivity produced in Substances by the Action of Thorium Compounds. By E. RUTHERFORD, M.A., B.Sc., Macdonald Professor of Physics, McGill University, Montreal \*.

THORIUM compounds under certain conditions possess the property of producing temporary radioactivity in all solid substances in their neighbourhood. The substance made radio-active behaves, with regard to its photographic and electrical actions, as if it were covered with a layer of radio-active substance like uranium or thorium. Unlike the radiations from thorium and uranium, which are given out uniformly for long periods of time, the intensity of the excited radiation is not constant, but gradually diminishes. The intensity falls to half its value about eleven hours after the removal of the substance from the neighbourhood of the thorium. The radiation given out is more penetrating in character than the similar radiations emitted by uranium and thorium and the radio-active derivatives from pitchblende, radium †, and polonium ‡.

Attention was first drawn to this phenomenon of what may be termed "excited radioactivity" by the apparent failure of good insulators, like ebonite and paraffin, to continue to insulate in the presence of thorium compounds.

The apparatus first used is shown in fig. 1.

Two insulated plates, B and C, were placed parallel to one another. In a shallow square depression LM in the plate C,

\* Communicated by Prof. J. J. Thomson, F.R.S.

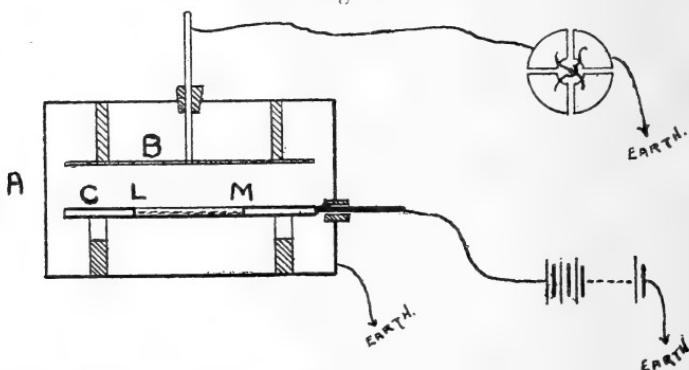
† Curie, C. R. 1898, p. 175.

† Curie, ibid. 26 Dec. 1898.

Phil. Mag. S. 5. Vol. 49. No. 297. Feb. 1900. M

a layer of thorium oxide was placed and covered with several layers of foolscap-paper. The whole was enclosed in a lead vessel A, with a door in the side to allow the plate C to be

Fig. 1.



readily moved. The crossed lines show the position of insulators. The plate C was connected to the + pole of a battery of 50 volts, the other terminal of which was to earth. The plate B was connected to one pair of quadrants of a delicate Thomson electrometer with a replenisher and gauge, the other pair of quadrants of which was connected to earth.

With the arrangement in the figure, when B is insulated, there can be no conduction-current from C along or through the insulators, since the earth-connected vessel intervenes. If the thorium-covered plate C was removed, and a brass one of the same dimensions substituted, there was no appreciable movement of the electrometer-needle. If, however, the plate C, covered with thorium oxide, were left in the vessel for several hours with the plate B charged —, on removal of C and the substitution of a non-active metal plate, the movement of the electrometer-needle showed that B was receiving a + charge. On reversing the battery, the current was reversed in direction but equal in amount. The current between the plates gradually decreased with the time, and became inappreciable after a few days. By replacing the thorium oxide, the experiment could be repeated.

It was at first thought that possibly dust particles from the thorium oxide might have escaped from under the paper and in some way adhered to the upper plate. An examination of the plate B, however, revealed no trace of thorium oxide on its surface. The plate made the air a conductor in its neighbourhood, as if it were covered with a thick layer of radio-active substance. If the surface of the plate was care-

fully scrubbed with sand- or emery-paper, the radio-active power was to a great extent destroyed. It was found possible to make the plate B active, even if the thorium oxide were covered with 30 layers of foolscap paper tightly waxed down so as to prevent the escape of dust particles.

If the plate C was charged — and B +, the plate B no longer became radio-active, but the top layer of paper over the thorium was found to be active on its upper side to about the same extent as the plate B in the previous case; *i.e.*, the negatively charged surface was made active in both cases.

All the compounds of thorium examined have the power of causing radioactivity in substances. The oxide, however, gives far the largest effects, and has consequently been used in most of the experiments.

The thorium compounds used were supplied by Messrs. Eimer & Amend, New York. The oxide was obtained by igniting the nitrate which had been manufactured from monazite sand. If the oxide is heated for some hours to a white heat in a platinum crucible, it loses its power of exciting radioactivity in substances to a very large extent.

#### *Comparison of Intensities of Radiation.*

The intensity of the radiation, excited in substances in the manner described, was in all cases compared by the electrical method. In general, for the purposes of measurement, the radioactivity was excited in flat plates or circular cylinders.

For flat plates the testing apparatus was similar to fig. 1. The brass plates corresponding to B and C were 5 cms. apart, with a potential-difference of 50 volts between them. The current between the plates, measured by the rate of movement of the electrometer-needle, was taken as proportional to the intensity of the radiation at the surface. With radio-active cylinders, the active cylinder was placed in a larger cylinder and concentric with it. The current for 50 volts between the cylinders was taken as a measure of the intensity of the radiation at the surface.

For experiments, extending in some cases over several days or weeks, it was necessary that for each observation the electrometer should be of the same degree of sensitiveness. This was roughly ensured by the Thomson Replenisher and Gauge, attached to the electrometer. For small variations from the standard sensitiveness, the values of the current were corrected by observing the number of divisions on the electrometer-scale corresponding to the E M.F. of a Clark cell.

As in the course of this paper it will be necessary to compare

the intensity of the radiation from radio-active plates and cylinders, a brief theoretical discussion will be given of the relation that exists between the intensity of the radiation, the area of the active surface, and the maximum current through the gas.

Two cases will be considered—

- (I.) When the radiation is given out uniformly from a plane surface and the current through the gas is measured between two parallel planes.
- (II.) When the radiation is given out from a cylinder and the current measured between concentric cylinders.

*Case I.*—We will first consider the case of a uniformly radio-active plate C, of area S, which is placed between two large parallel plates A and B (fig. 2 a).

Fig. 2 a.

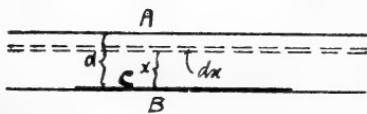
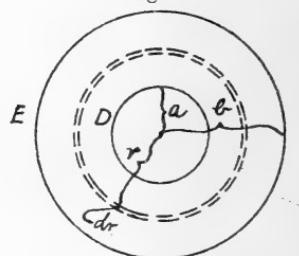


Fig. 2 b.



We will suppose the plate C to be of large dimensions compared with the distance  $d$  of the plate C from A, and to give out radiation equally from all points of its surface. The gas is ionized by the passage of the radiation through it, and the ions produced travel to the plates A and C under the influence of the electric field.

In consequence of the energy required to ionize the gas, the intensity of the radiation diminishes in its passage through it.

Suppose the radiation is homogeneous in character, and that  $\lambda$  is the coefficient of absorption of the radiation by the gas. Let  $I_0$  be the intensity of the radiation at the surface of the plate. Since the plate is large compared with the distance  $d$ , the value of the intensity may be considered approximately equal at equal distances from the surface C. In consequence of the absorption of the radiation by the gas, the intensity  $I$  at a distance  $x$  from the active plate is given by

$$I = I_0 e^{-\lambda x}.$$

Let  $dn$  be the number of ions produced per second between two planes parallel to C and distant  $x$  and  $x+dx$  from it.

Since the rate of production of ions is proportional to the

intensity of the radiation, the total number of ions  $n$  produced per second between A and C, distant  $d$  apart, is given by

$$n = \int_0^d K S I_0 e^{-\lambda x} dx, \text{ where } K \text{ is a constant,}$$

$$= \frac{K S I_0}{\lambda} (1 - e^{-\lambda d}).$$

If  $\epsilon$  is the charge on an ion, the current  $i$  through the gas, when an E.M.F. is applied sufficient to remove all the ions before recombination takes place, is given by

$$i = n\epsilon.$$

Therefore

$$S I_0 = \frac{i\lambda}{K\epsilon(1 - e^{-\lambda d})};$$

or the product of the intensity of the radiation and the area of the active surface is proportional to the current through the gas.

It is of interest to develop the above equation from considerations of the energy required to produce an ion.

Let  $W$  be the average amount of energy used up in producing an ion in the gas. We will assume that the absorption of the energy of the radiation in its passage through the gas is due solely to the production of ions. On account of the absorption, the intensity of the radiation varies from  $I_0$  at the surface of the active plate to  $I_0 e^{-\lambda d}$  at the surface of the top plate. If  $n$  be the total number of ions produced, we thus obtain

$$n \cdot W = S I_0 (1 - e^{-\lambda d}),$$

where the energy absorbed over an area  $S$  is given by the right-hand side of the equation ; or

$$S I_0 = \frac{W i}{\epsilon(1 - e^{-\lambda d})},$$

where current  $i = n\epsilon$ , as before.

Some experiments given in previous papers\* point to the conclusion that the energy required to produce an ion may possibly be the same for all gases at all pressures, and it has been shown by Prof. J. J. Thomson and Mr. Townsend that the charge of the ions † in different gases is the same. If such is the case,  $W/\epsilon$  is a constant for all gases and the current through the gas will depend only on  $\lambda$ ,  $d$ , and  $S I_0$ .

\* Rutherford, Phil. Mag. Jan. 1899.

† J. J. Thomson, Phil. Mag. Dec. 1898; J. S. Townsend, Trans. Roy. Soc. 1899.

*Case II.*—We will now consider the case of a radio-active cylinder, where the current is measured between two concentric cylinders. Let fig. 2 b represent a cross-section of the cylinders. Let  $a$ =radius of radio-active cylinder D,  $b$ =radius of concentric cylinder E. Suppose length of cylinder D to be large compared with the distance between the cylinders. If  $\lambda$  is the coefficient of absorption of the radiation, the intensity I at a distance  $r$  (outside D) from the centre is easily seen to be

$$\frac{I}{I_0} = \frac{a}{r} e^{-\lambda(r-a)},$$

where  $I_0$ =intensity of radiation at the surface, since without any absorption the value of I would fall off inversely as the distance. The total energy of the radiation near the surface of the external cylinder is given per unit length by

$$I_0 \frac{a}{b} e^{-\lambda(b-a)} \cdot 2\pi b,$$

the energy per unit length close to the surface of the active cylinder by  $I_0 \cdot 2\pi a$ .

The total energy absorbed in the gas is thus equal to

$$I_0 \cdot 2\pi a \{1 - e^{-\lambda(b-a)}\}.$$

If  $n$ =the number of ions produced per second due to the length  $l$  of the active rod,

$$\begin{aligned} W \cdot n &= I_0 \cdot 2\pi al \{1 - e^{-\lambda(b-a)}\} \\ &= I_0 \cdot S \{1 - e^{-\lambda(b-a)}\}, \end{aligned}$$

where S is surface-area of active cylinder ;

$$\begin{aligned} \text{or } SI_0 &= \frac{W \cdot i}{\epsilon \{1 - e^{-\lambda(b-a)}\}}, \text{ where } i = n\epsilon, \\ &= \frac{Ai}{1 - e^{-\lambda(b-a)}}, \text{ where } A = \frac{W}{\epsilon} = \text{constant}. \end{aligned}$$

In both of the cases considered, half the radiation has been absorbed in the substance which is made radio-active, and the other half passes through the gas, since the radiation is given out from the surface in all directions. In the case of complete absorption of the radiation in the passage through the gas, the maximum current  $i$  is given by

$$SI_0 = Ai.$$

An investigation is now in progress to determine the value of A, that is,  $W/\epsilon$ . If A is determined, the intensity of the radiation can at once be expressed in absolute measure.

*Conditions for the Production of Radioactivity in Substances.*

In order to *confine* the induced radioactivity produced by thorium compounds to any particular conductor, it is necessary that it should be charged — and all other bodies in the field +. In order to produce radioactivity in all bodies in the neighbourhood, no electric field is required. If thorium oxide is placed in a closed vessel connected to earth, the sides of the vessel and any solid bodies near, whether conductors or insulators, become radio-active. If, in addition, the surface of the thorium oxide is covered with paper or thin aluminium-foil, the side of the paper away from the oxide becomes radio-active. When no electromotive forces are acting, the amount of radioactivity in a given time per unit area is greater the nearer the body to the thorium oxide.

With electromotive forces acting, the substance to which the radioactivity is due appears to travel along the lines of force from the + to the — charged body. It is thus possible to *concentrate* the radioactivity on small plates or fine wires by placing them in a closed metal vessel connected to earth and charging them —.

If the bodies are all uncharged, the particles producing radioactivity, by the process of diffusion through the gas, are carried to the sides of the bodies and adhere to them. A fine wire fixed in the centre of a vessel on the bottom of which the active salt is placed becomes only slightly radio-active, since only a few of the active particles reach its surface. The closer a body is to the thorium, other conditions remaining unaltered, the more active it becomes.

Fig. 3.

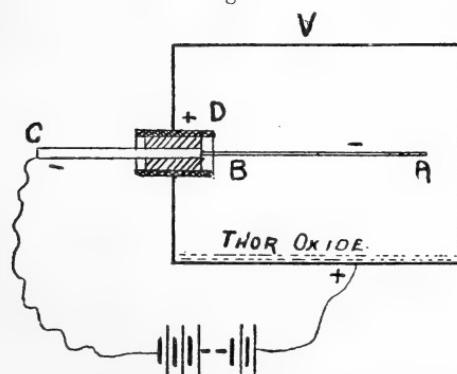


Fig. 3 shows the general arrangement for concentrating the activity on a small area of a conductor. A metal vessel V

was connected to the + pole of a battery of small lead accumulators of 300 volts, the other pole of which was to earth.

A thick layer of thorium oxide was placed in the bottom of the vessel and covered with several thicknesses of paper. A brass tube D was fixed in the side of the vessel and metallically connected with it. A fine platinum wire AB was fixed on the end of a stouter brass rod BC. The brass rod was fixed centrally in the cylinder D and insulated from it. The end of the brass rod B was placed well inside the cylinder D. The conductor AC was connected to earth.

The fine wire is thus the only body exposed in the field, with a charge, and, under the influence of electric forces, the active particles are carried to the wire AB and adhere to its surface.

The same general results are obtained whether the surface of the thorium oxide is bare or covered with paper or thin layers of metal-foil.

Two or three layers of paper almost completely cut off the ordinary radiation \* from thorium; so the effect cannot be due to the direct radiation from its surface.

In this way I have been able to cause a piece of platinum wire of length 1 cm. and diameter .018 cm., *i. e.* with a surface area of .056 cm., to give more than 20 times the rate of discharge given by a thick layer of uranium oxide of 25 sq. cms. area. A rate of movement of an electrometer-needle of 200 divisions in 5 seconds is quite easily obtained from the action of such a small active surface. (1 volt gave a deflexion of 40 divisions on the electrometer-scale, and the capacity of the whole circuit was about 50 electrostatic units.)

I have spoken of using a platinum wire, but any other metal wire will serve equally well. Using large electro-motive forces and a large surface of thorium oxide, it would be quite possible to increase the radioactivity of unit area of the conductor to more than 20 times the value cited in the above case. So far as the results obtained indicate, there is no limit to the amount of increase, since we can suppose the area of the — charged conductor diminished and the amount of thorium increased. In practice, however, a limit would soon be reached, as it would be difficult to cause all the radio-active particles to move to the small conductor without very large electric forces.

\* E. Rutherford, Phil. Mag. Jan. 1900.

*Connexion between the "Emanation" from Thorium and  
"Excited" Radio-activity.*

In a previous paper\* I have shown that compounds of thorium emit some kind of radio-active material or "emanation," which is able to pass through considerable thicknesses of paper and thin layers of metal, and preserves its radiating power for several minutes. These particles diffuse through the gas and become centres of ionization throughout the volume of the gas. The current passing between two charged plates, on one of which is spread thorium oxide, is greatly diminished by directing a slow continuous blast of air between the plates. As the particles have no charge, they may be readily removed from between the plates by a current of air even in a strong electric field.

There is a very close connexion between this "emanation" and excited radioactivity—in fact, the emanation is in some way the direct cause of the latter. The following facts will serve to show the close connexion that exists :—

(1) All thorium compounds examined are able to make substances radio-active, but to different degrees. The greater the amount of emanation, the greater the amount of induced radioactivity. As an example, thorium oxide is the most active of all thorium compounds in producing radioactivity and giving out the emanation. A thin layer of thorium oxide gives out very little emanation, and is only slightly effective in producing radioactivity.

(2) Substances are made radio-active when the active compound is covered with several layers of paper or thin metal foil. The emanation also readily passes through paper and thin metal foil. Two or three layers of ordinary foolscap-paper completely cut off the ordinary radiation given out by thorium compounds, but do not much diminish the amount of induced radioactivity.

(3) A slow current of air, which quickly removes the emanation as it appears, also diminishes the power of producing radioactivity. The amount of induced radiation is greater in closed than in open vessels, on account of the disturbance of air-currents in the latter case.

(4) Thorium oxide which had been heated to a sufficiently high temperature gave out very little emanation and produced little radioactivity.

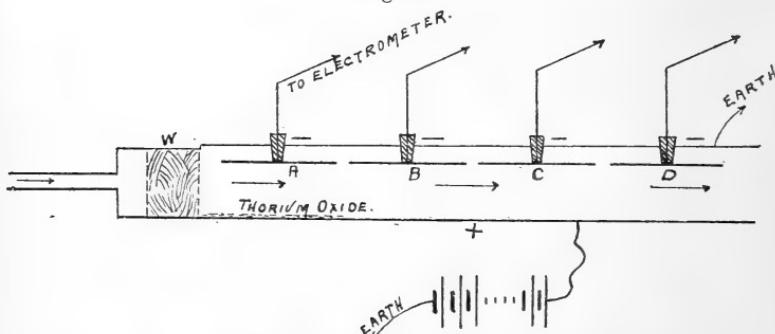
Speaking generally, it may be said that the presence of the emanation is necessary for the production of radioactivity in

\* Phil. Mag. January 1900.

substances, and that the amount of radioactivity depends upon the amount of the "emanation." A radio-active substance like uranium, which gives out no emanation, produces no trace of excited radioactivity.

An experiment now to be described throws a further light on the question. The general arrangement of the experiment is shown in fig. 4.

Fig. 4.



A slow current of air from a gas-bag, after bubbling through sulphuric acid, passed down through a rectangular wooden vessel, 60 cms. in length. In order to remove spray and dust and to equalize the current of air over the cross-section, the air was passed through cotton-wool at W. A metal plate covered the bottom of the vessel and was charged +. Four insulated metal plates, A, B, C, D, placed at equal distances, were attached to a top metal plate connected to earth. Thorium oxide covered with paper was placed under the electrode A.

The current of air was passed through the vessel at the steady rate of about 2 cm. per second for a period of 7 hours, with 300 volts between the lower and upper plates. The following results were obtained for the current due to the emanation which reached A, B, C, D and the corresponding radioactivity produced :—

	Relative current due to emanation.	Relative excited radioactivity.
Plate A . . .	1	1
" B . . .	.55	.43
" C . . .	.18	.16
" D . . .	.072	.061

The current due to the emanation which reaches A, and the radioactivity produced in A, is in each case taken as unity for

the purpose of comparison. It will be observed that radioactivity is produced on the plates some distance away from the thorium oxide, and is roughly proportional to the emanation-current at the plate. We may conclude from this experiment that the radioactivity is, in some way, due to the "emanation," or to something that accompanies it, but is not caused by the direct action of a radiation from thorium oxide.

*Absorption of the Radiation by Substances.*

All radio-active substances, as well as bodies made radioactive in the manner described, ionize the gas in their neighbourhood and act upon a photographic plate in the dark. A simple method of testing whether two types of radiation are the same, is to determine the absorption of the radiation by layers of thin metal foil. If the absorption is different for the two types of radiation, we may consider them distinct kinds of radiation.

The current between two parallel plates, one surface of which was radio-active, was determined when successive layers of a substance of equal thickness were placed over the radioactive plate. The following table is an example of the way the current (which is proportional to the intensity of the radiation) diminishes with successive layers of aluminium-foil over a plate of zinc, which had been made radio-active :—

Zinc plate =  $12 \times 18$  cms.

Thickness of foil = .0004 cm.

95 volts between plates.

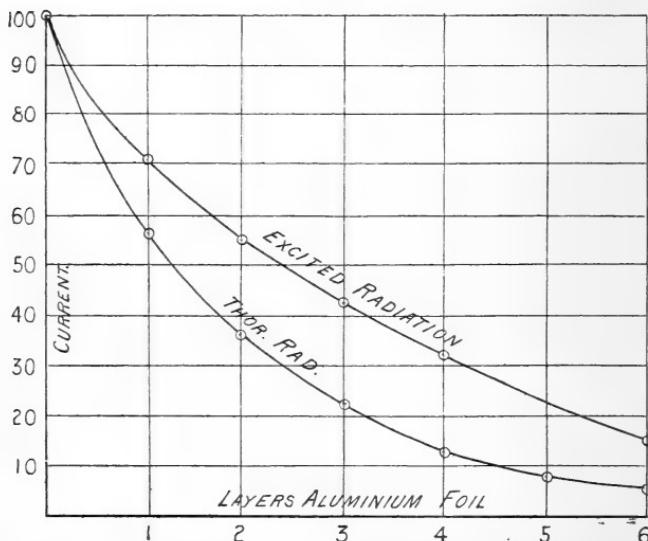
No. of layers alum. foil:	Current for radia- tion from zinc.	Current for thin layer of thorium oxide.
0	1	1
1	.71	.57
2	.55	.36
3	.43	.23
4	.32	.13
5	...	.084
6	.155	.056

The third column of the table gives the variation of the current with thickness of foil for a *thin* layer of thorium oxide, and serves as a basis of comparison with the excited radiation. The current for the bare radio-active surface is in each case taken as unity for the purpose of comparison.

Fig. 5, curves A, B, show these results graphically when the ordinates denote current and the abscissæ thicknesses of aluminium.

It will be observed that the radiations from zinc and thorium oxide are quite different in character, the radiation from the former being far more penetrating as regards aluminium. Both types of radiation are approximately homogeneous. The current, which is proportional to the intensity of the radiation, diminishes approximately in a geometrical progression as the thickness of the metal increases in arithmetical progression.

Fig. 5.



The same general difference is shown for the two types of radiation by testing their comparative absorption by thin layers of paper, gold-leaf, silver-foil, and Dutch metal.

The following table is an example of the absorption of the radiation from a zinc plate and a thin layer of thorium oxide for thin tissue-paper:—

Thickness of layer of paper = .0030 cm.

Potential-difference between plates = 50 volts.

#### Current.

No. of layers of paper.	Radiation from zinc.	Radiation from thorium oxide.
0	1	1
1	.57	.37
2	.35	.16
3	.20	.080
4	.12	.055

This method can also be used to compare the radiations from the various metals when made radio-active. In this way it was found that all the substances tried, viz., Cu, Pb, Pt, Al, Zn, brass, cardboard, paper, which had been made radio-active, gave out radiations of the same penetrating power. It was also found that the same type of radiation was given out from polished and dull surfaces, and that it was unaffected by the concentration of the radioactivity.

Since the same radiation is given out by all the metals and non-metallic substances like cardboard or paper, under varying conditions, we may conclude that either the substance itself which has been made radio-active plays no direct part in determining the kind of radiation, or that all exert exactly the same action.

The "excited" radiation is also of a more penetrating character than that given out by uranium, thorium, and the pitchblende derivatives radium and polonium.

#### *Absorption of the Radiation in Air.*

The absorption of the induced radiation in air was also determined. The method employed was similar to one previously used and described by the author \* for determining the absorption of uranium radiation by different gases. A similar apparatus has been employed by Owens † for thorium radiation.

Two insulated parallel plates, kept a fixed distance apart, could be moved by means of a screw to different distances from the parallel radio-active surface. The radiation from the active surface passed through a circular opening in the lower plate, covered with thin aluminium-foil, and was stopped by the upper plate. The current between the two fixed plates for a large voltage was determined for different distances from the radio-active plate. If the radius of the active surface is large compared with the distance of the lower of the pair of plates from it, the current between the plates for a distance  $x$  of the lower plate from the active surface varies as  $e^{-\lambda x}$ , where  $\lambda$  is the coefficient of absorption of the radiation in the gas.

The following table gives the results obtained for the radiation from a lead surface which had been made strongly radio-active ;—

\* Phil. Mag. Jan. 1899, p. 124.

† Ibid. Oct. 1899, p. 378.

## Lead Radiation.

Distance from surface.	Current.
$d (=3 \text{ mms.})$	1
$d+6.25 \text{ mms.}$	.79
$d+12.5 \text{ "}$	.59
$d+18.7 \text{ "}$	.46
$d+25 \text{ "}$	.35
$d+31.2 \text{ "}$	.27
$d+37.5 \text{ "}$	.21

The current is taken as unity when the measurements began at a distance  $d=3$  mms. from the active lead plate.

For the purposes of comparison, the numbers obtained in a similar manner for thin layers of thorium oxide and uranium oxide on a bare plate are given below.

## Thorium Radiation.

## Uranium Radiation.

Distance.	Current.	Distance.	Current.
$d (=2.25 \text{ mms.})$	1	$d (=2.25 \text{ mms.})$	1
$d+5 \text{ mms.}$	.73	$d+2.5 \text{ mms.}$	.685
$d+10 \text{ "}$	.50	$d+5 \text{ "}$	.445
$d+15 \text{ "}$	.35	$d+7.5 \text{ "}$	.296
$d+20 \text{ "}$	.25	$d+10 \text{ "}$	.188
		$d+15 \text{ "}$	.088
		$d+20 \text{ "}$	.059

The curves in fig. 6 show the results graphically. It will be seen that the intensity of the radiation falls off approximately in a geometrical progression as the distance increases in arithmetical progression. Curves of absorption of thorium radiation in air at different pressures have been obtained by Owens \*.

The distances through which the three types of radiation from uranium, thorium, and active lead pass through air at ordinary pressures and temperatures before the intensity is reduced to one-half its value, are about 4, 10, and 16.5 mms. respectively.

\* Owens, Phil. Mag. Oct. 1899.

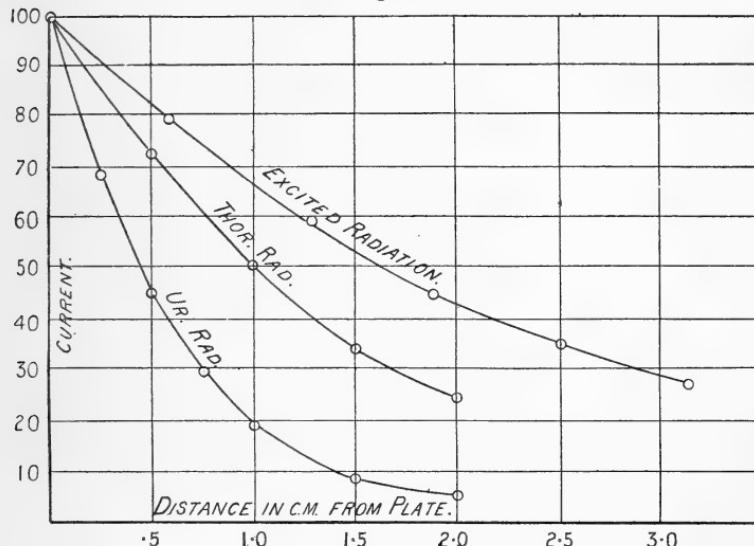
Assuming that the intensity falls off as  $e^{-\lambda x}$ , the values of  $\lambda$  for the types of radiation are given below.

	Value of $\lambda$ .
"Excited" radiation . . . . .	·42
Uranium . . . . .	1·6
Thorium . . . . .	·69

The order of absorption in air of the above three types of radiation is the same as for aluminium and paper.

The "excited" radiation is of a more penetrating kind than the easily absorbed type (the  $\alpha$  radiation) \* given out by uranium, but much less than the  $\beta$  type. The radiations from radium and polonium are also more readily absorbed in air than the excited radiation is.

Fig. 6.



#### Duration of the Radioactivity.

If a plate or wire which has been made radio-active is removed from the action of the thorium, the intensity of the radiation diminishes according to a very simple law.

A large number of experiments have been made on the duration of the induced radioactivity in various substances under varying conditions. A typical table of the results obtained is given below for a rod of brass which has been

\* Rutherford, Phil. Mag. Jan. 1899, p. 116.

made active. In order to test the rate of decay of the intensity, the active rod was placed inside a cylinder and concentric with it. The current between the two cylinders for a potential-difference of 50 volts was measured in the usual manner, and at intervals of several hours.

Length of rod = 31.5 cms.

Diameter = .40 cms.

Testing-cylinder, inside diameter = 7.3 cms.

Time in hours.	Current.
0	1
7.9	.640
11.8	.474
23.4	.196
29.2	.138
32.6	.103
49.2	.0370
62.1	.0186
71.4	.0086

The value of the maximum current, which is taken as unity, was  $1.6 \times 10^{-11}$  amperes.

Fig. 7 shows graphically the results obtained. The results show that the current through the gas (which is proportional to the intensity of the radiation) diminishes in geometrical progression with the time. The time taken for the intensity of the radiation to fall to half its value is about eleven hours. If  $I_0$  be the intensity at the beginning, the intensity  $I$  after a time  $t$  is given by

$$I = I_0 e^{-Lt},$$

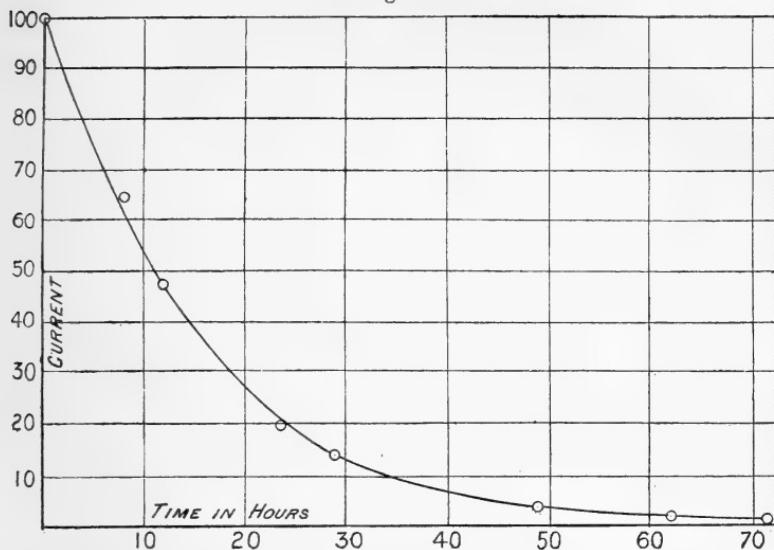
where  $L$  is a constant.

The above law appears to hold accurately for all substances made radio-active. No difference in the rate of decay has been observed, whether the radiation is on a plate of large area or concentrated on a fine wire. The rate of decay is also independent of the substance made radio-active. A piece of paper, mica, or metal, all give the same rate of loss of intensity. As far as experiments have gone, the rate of decay is unaffected by the pressure of the gas surrounding it, or whether the air is dry or full of moisture. The same rate of decay has always been obtained under all the conditions tried, provided the surface is not acted on mechanically or by chemicals.

The mean value of  $L$  deduced from the above results is

$$L = .0000189,$$

Fig. 7.



In a previous paper \* I have shown that the radio-active "emanation" from thorium compounds quickly loses its radio-active power.

The intensity in that case falls to half its value in about one minute, while the intensity of the "excited" radiation falls to half its value in about eleven hours, or one decays 660 times faster than the other. The law of falling off of intensity is the same in the two cases.

On page 166 it has been shown that the current  $i$  (for a "saturating" E.M.F.) between two cylinders is given by

$$i = \frac{SI_0}{A} \{1 - e^{-\lambda(b-a)}\},$$

with the same notation as before.

The intensity  $I$  of the radiation after a time  $t$  is given by

$$I = I_0 e^{-\lambda t},$$

and the total quantity of electricity passing between the cylinders during the time taken for the intensity to fall to zero is given by

$$\begin{aligned} Q &= \int_0^{\infty} idt = \frac{SI_0}{A} \{1 - e^{-\lambda(b-a)}\} \int_0^{\infty} e^{-\lambda t} dt \\ &= \frac{SI_0}{\lambda A} \{1 - e^{-\lambda(b-a)}\}; \end{aligned}$$

\* Phil. Mag. Jan. 1900.

if  $i_0$ =initial current, it is clear that

$$Q = \frac{i_0}{L}.$$

In the case given in the last table, the initial current was  $1.6 \times 10^{-11}$  amperes, and the value of  $L=0.0000189$ ; therefore the total quantity of electricity passing between the cylinders is equal to  $8.5 \times 10^{-7}$  coulombs.

The total quantity of electricity separated, if the radiation has been completely absorbed in the gas, is obviously

$$\frac{1}{1 - e^{-\lambda(b-a)}}$$

of this quantity.

In the above case,  $a=20$  cm.,  $b=3.65$  cms.,  $\lambda=42$ .

Therefore quantity passing between cylinders  $= 11.1 \times 10^{-7}$  coulombs.

#### *Increase of Induced Radioactivity with Time.*

If a plate or wire is exposed to the action of thorium oxide in a closed vessel, the radioactivity at first increases nearly proportionally with the time, and then more slowly, finally tending to a maximum value after several days' exposure.

The table given below is an example of the results obtained for a square zinc plate, area 86 sq. cms., exposed in a metal vessel, with a potential-difference of 300 volts between thorium and surface to be made active. The plate was removed from the action of the thorium at intervals for sufficient time to determine the current produced by it between two charged parallel plates, as in fig. 1.

Time of exposure in hours.	Current.
1.58	.063
3.25	.105
5.83	.289
9.83	.398
14.00	.586
23.41	.773
29.83	.834
47.00	.898
72.50	.951
96.00	1.00

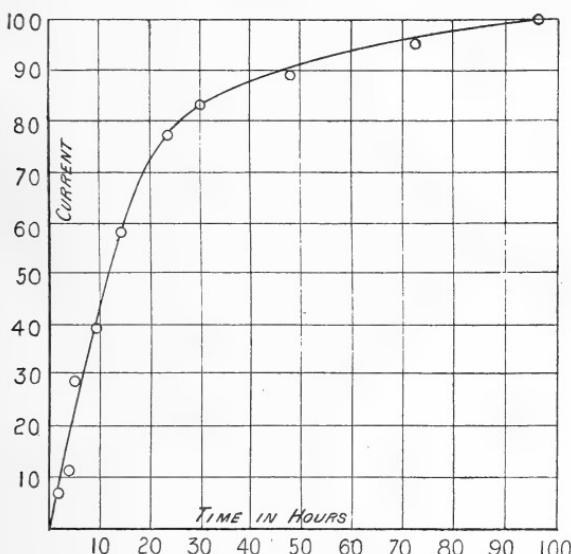
The current after four days' exposure is taken as unity, as the rate of leak had nearly reached its maximum value.

The maximum value of the current produced by the active

plate between two test-plates 4 cms. apart was  $1.7 \times 10^{-11}$  amperes.

Fig. 8 shows the results graphically. From the table it will be seen that the intensity has reached half its final value in about twelve hours.

Fig. 8.



We will now consider the conditions which influence the increase of the intensity of radiation from a given surface exposed to the action of a thorium compound. We will suppose that the surface to be made radio-active is negatively charged.

Two opposing actions are evidently at work. Fresh radioactive particles are being continually carried to the plate, while the intensity of the radiation given out by the active surface continually diminishes, owing to the radiation of energy. A steady state will be reached when the rate of increase of intensity due to the supply of fresh radio-active particles is equal to the rate of decrease of the intensity due to the radiation of energy from the active surface.

Let  $I$  be the intensity of the radiation at the surface of the plate at any time. The rate of diminution of the intensity is equal to  $LI$ , since the intensity  $I$  at any time is given by

$$I = I_0 e^{-Lt}$$

and

$$\frac{dI}{dt} = -LI.$$

Let  $q$  be the rate of increase of the intensity due to the steady supply of radio-active material. Then

$$\frac{dI}{dt} = q - LI$$

or

$$\log_e(q - LI) = - Lt + A.$$

But  $I=0$  when  $t=0$ .

Therefore

$$A = - \frac{1}{L} \log_e q.$$

Therefore

$$\log_e \frac{q - LI}{q} = - Lt$$

or

$$I = \frac{q}{L} (1 - e^{-Lt}).$$

When  $Lt$  is very large, the maximum value of the intensity  $I_0$  is given by

$$I_0 = \frac{q}{L} \quad \text{and} \quad \frac{I}{I_0} = 1 - e^{-Lt};$$

or the equation representing the rise of intensity of the radiation is the same as the rise of an electric current in a circuit of constant self-induction.

The curve which is shown in fig. 8 is in rough agreement with this equation. For example, the intensity of the radiation has risen to half its value in about twelve hours. Now  $e^{-Lt} = \frac{1}{2}$  when  $t = 11$  hours, *i.e.*, according to theory, the current should have reached half its value in about eleven hours.

There is a divergence between the theoretical and observed results in the first part of the curve. The rate of increase of intensity is slower at first than the theory would suggest. It is probable, however, that the rate of supply of radio-active material does not reach a steady value for a considerable time after the exposure of the plate, and such a cause would account for the results observed. Other results obtained, under different conditions, all show too small a value of the intensity for the first few hours of exposure.

We have so far assumed that the radio-active particles were conveyed to the surface under the influence of an electric field. The equations which have been given will, however, apply equally well to the case of diffusion. If no electromotive forces are acting, the radio-active particles

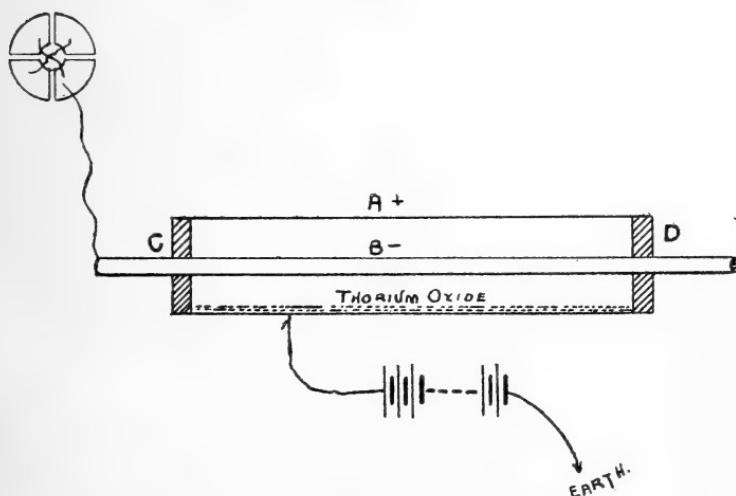
diffuse through the gas and adhere to the surface on which they impinge. A steady state will be reached when the rate of supply of fresh radio-active particles due to diffusion is balanced by the decay of the radiation from the surface. The maximum intensity of the radiation on any surface in the neighbourhood of a thorium compound is thus proportional to the number of radio-active particles that reach it by the processes of diffusion.

#### *Effect of E.M.F. on the Amount of Radioactivity.*

The amount of induced radioactivity in a given time increases with the voltage for small voltages, but soon reaches a point beyond which large increases in the E.M.F. have a very small effect on it. In order to investigate the relation in detail, the following arrangement was employed :—

Two insulated concentric brass cylinders A and B (fig. 9) were used, of diameters 5·5 and ·7 centim. respectively. The

Fig. 9.



ends were closed with paraffin stoppers C and D. The cylinder A was connected with the + pole of a battery, the other pole of which was to earth. The cylinder B was connected to the electrometer in the usual manner. A layer of thorium oxide in a paper envelope was placed along the bottom of the cylinder A. The whole was exposed to the action of thorium oxide for three days. The intensity of the radiation given out by B had, after that interval, nearly reached its maximum value.

The following measurements were made for each experiment at different voltages :—

- (1) The current between A and B was measured with the thorium oxide in the cylinder.
- (2) After the thorium oxide had been removed and the air blown out, the current between A and B was again determined.
- (3) The cylinder B was then removed and a non-active one of the same dimensions substituted and the current again observed.

The electrometer was brought to the same sensitiveness every day by means of a Thomson Replenisher. For rapid rates of discharge, a condenser of .001 microfarad capacity was placed in the electrometer circuit.

The current (3) includes the small leak (if any) over the insulators plus the current due to the radioactivity produced in the end paraffin stoppers. The current (2) was due to the radio-active cylinder B, together with the current (3). The current (1) was due to the "emanation" from thorium oxide plus (2) and (3).

From these three observations it was therefore possible to determine :—

- (a) The rate of discharge due to the thorium alone ;
- (b) The rate of discharge due to radio-active cylinder B alone ;
- (c) The rate of discharge due to radioactivity on the sides and ends of vessel.

In the following table the results are given for different voltages between cylinders.

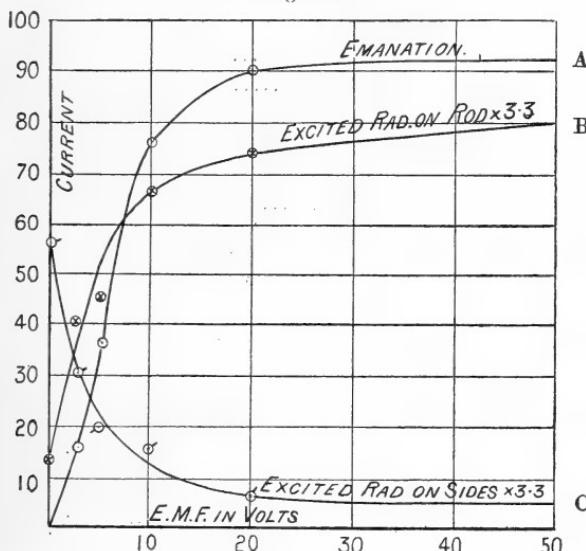
Results are in divisions per second of electrometer-scale.

Voltage.	Emanation.	Radioactivity. on cylinder B.	Radioactivity on sides and ends.	Total Radioactivity.
0	.....	1.32	5.58	6.90
3	5.3	4.02	3.06	7.08
5	12.2	4.53	1.97	6.50
10	25.3	6.69	1.51	8.20
20	30.0	7.40	.59	7.99
310	32.2	9.91	.75	10.66

Fig. 10 shows the results graphically. Curve A shows the variation of the current due to the "emanation" with voltage ;

curve B, the variation of the amount of induced radioactivity on inside cylinder; and curve C, the variation of the amount of radioactivity on the sides and ends. The ordinates of curves B and C are increased three times in order to show them on about the same scale as A. It will be observed that the shapes of the curves A and B are similar. The "knee" of both curves occurs for about the same voltage. The

Fig. 10.



curve C shows that as the voltage diminishes, the amount of radioactivity on the sides and ends increases, reaching a maximum when the voltage is zero. The currents due to the radioactivity of B, given in the third column of the table, are for 50 volts between the cylinders. The value given for 310 volts is probably too large, as it was measured for 310 volts between plates, instead of 50 as in the other experiments.

In the fifth column is given the total current due to the radioactivity on ends and sides plus the action of cylinder B. It will be observed that the resulting values are not very different, except the value for 310 volts, which, for reasons above explained, is probably too large.

It looks as if a certain number of radio-active particles were given out from the thorium and that these were carried to various parts of the vessel, the effect due to the whole number being about the same as if they were all concentrated on the negative electrode.

*Case of Diffusion of Radio-active Particles.*

The case where no voltage is acting is one of special interest, for there the diffusion of the radio-active particles is alone operative. A loose layer of paper was placed over the paper envelope containing the thorium oxide. The paper envelope bent into the arc of a circle covered about one quarter of the circumference of the cylinder. The following numbers give the rate of leak, in divisions per second, due to the radioactivity on different portions of the vessel :—

Radioactivity on inside cylinder	... 1·32	divisions per sec.
"    on paper .....	2·26	"
"    on outside cylinder } and stoppers     }	3·32	"
Total radioactivity .....	6·90	"

The current due to the total radioactivity is thus about the same as the current when 20 volts acts between cylinders. The experiments on the effect of voltage extended for more than a month, and some of the results showed that the thorium oxide was not a constant source of radiation during the whole of that time. The variations were not, however, sufficiently large to obscure the general nature of the results.

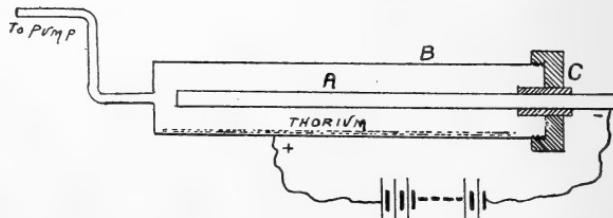
*Effect of Pressure on Radioactivity.*

The diminution of the pressure of the gas from 760 to 20 millim. had very little action on the amount of "excited" radioactivity on the — charged electrode.

The following apparatus was employed :—

A brass cylinder B (fig. 11 *a*), with an ebonite stopper C,

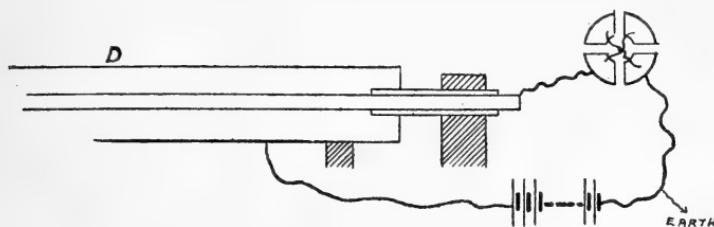
Fig. 11 *a*.—Exciting Apparatus.



through which passed a brass rod A, was connected with a mercury pump.. The thorium oxide inside a paper envelope was placed inside the cylinder. B was connected to + pole of a battery of 50 volts, and C to — pole. The apparatus was

exhausted to the required pressure as rapidly as possible, and rod A exposed for several hours. The rod was then removed, and the current due to its radioactivity tested inside another cylinder D (fig. 11 b). The battery and electrometer

Fig. 11 b.—Testing Apparatus.



connexions are seen in figure. On account of the press of other work, it was not found possible to take observations at regular intervals, but the table given below suffices to show the general nature of the results.

Pressure.	Time of Exposure.	Divisions per second.	Divisions per sec. Interpolated values.
millim. 760	hours. 5·25	2·37	13·1
175	20	9·83	13·9
16	4·1	2·15	15·1
4·5	5·4	1·96	10·3
1·7	4·8	.72	4·5
.45	14·3	.38	.65
.04	25	.34	.44

The third column gives the current in divisions per second due to radio-active rod in the testing vessel. In the fourth column are given the divisions per second corresponding to an exposure of the rod for the same time (three days) in each case, at the particular pressure. The results are interpolated from the first two columns with the help of the curve given in fig. 8. The results must only be considered approximate, and merely serve to give a comparative estimate of the radioactivity at each pressure. The general results are clear. The radioactivity is about the same at 16 millim. as at 760 millim. Between the pressures of 16 and 4·5 millim. the amount begins to diminish, until at .45 millim. it is only  $\frac{1}{20}$  of the

value at atmospheric pressure. Still further diminution of pressure does not have much effect.

A special experiment on the distribution of the radioactivity at low pressures throws some light on the phenomena. If we expose a rod charged — at a low pressure to the action of thorium, it will be found that the rod is only slightly radio-active, while the top of the paper over the thorium oxide and the sides of the vessel are strongly radio-active. At atmospheric pressure, other conditions remaining the same, it will be found that most of the radioactivity is confined to the rod, and only a slight amount is produced on the paper and sides of the vessel. It appears as if the radio-active particles are unable to be all carried to the negative electrode at low pressures. This may be due to the increased rate of diffusion of the active particles at low pressures, or more probably to the small number of ions produced by the "emanation" at low pressures.

It is found that the current through the gas due to the "emanation" falls off nearly proportionally to the pressure, so that the number of ions present between cylinders at low pressures is a very small fraction of those at atmospheric pressure.

The following table gives results of the variation of the current, due to the emanation, with pressure of air in the apparatus of fig. 11 *a*.

Pressure of Gas. millim.	Current due to Emanation.
760	1
587	.819
402	.582
214	.297
145	.203
93	.133
25	.046

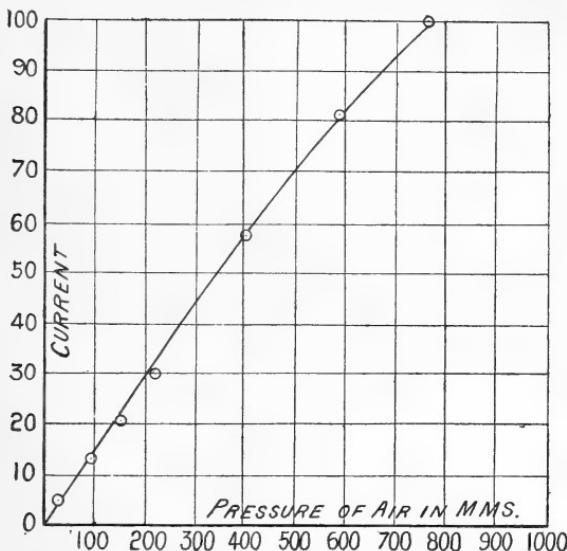
Fig. 12 shows the results graphically. The curve is nearly a straight line. If the conveyance of the radio-active particles to the electrode is due to the movements of the ions between cylinders, at low pressures the number of ions may be too small to be effective in that respect.

#### *Effect of Gases.*

The apparatus shown in fig. 11 was used. The amount of radioactivity produced on the central rod was not very different whether the gas was hydrogen, air, or carbonic acid.

No definite difference was observed whether the gas was free from water-vapour or not. The amount of current due to the emanation from thorium oxide was found, however, to vary

Fig. 12.



greatly with the gas. Taking the current due to air as unity with 50 volts acting, the currents due to the "emanation" were

Air .....	1
H .....	.35
CO <sub>2</sub> .....	1.1

These numbers are not necessarily proportional to the ionization constants of the gas, as the current produced depends on the relative absorption of the rays between the cylinders.

These results, together with those obtained for lowering of the pressure in air, show that there is no evident quantitative connexion between the current due to the emanation and the amount of induced radioactivity.

#### *Chemical and Mechanical Actions on the Radio-active Surface.*

We have previously considered the conditions which govern the production and decay of the induced radioactivity. We will now describe some experiments that have been made to

try and throw some light on the question as to what the induced radioactivity is really due to.

If the radioactivity is caused by some radio-active dust deposited on the substance, we should expect to find evidence of it by examining the surface with a microscope, or by noting whether there is any increase in weight. A fine piece of platinum wire, which had been carefully weighed, was made strongly radio-active by five days' exposure to thorium oxide covered over with paper. Within the limits of accuracy of the balance no certain variation of the weight could be detected. The increase of weight, if any, was certainly less than  $\frac{1}{20}$  of a milligramme. On examination by a microscope no collection of dust particles on the surface could be observed. We may conclude from this experiment, that if the radioactivity is due to the deposition of radio-active particles on the surface, these particles must be extraordinarily radio-active compared with their weight. A rough estimate shows that the radioactivity of the surface-layer must be at least a million times greater than that of uranium or thorium.

The amount of radiation from an active surface is always lessened by mechanical actions, such as rubbing the surface with a cloth or fine sand-paper. In order to completely remove the radioactivity, it is necessary to remove the surface-layer by long scouring with sand- or emery-paper.

A blast of air directed against a radio-active plate has no appreciable effect on the amount of radiation given out.

A radio-active platinum wire or plate can be heated white-hot without much altering the amount of radiation given out from it. A strongly active fine wire is more affected than a plate; but that is probably chiefly due to action of the flame-gases upon it.

#### *Chemical Actions.*

The radioactivity of a platinum plate is not much affected by dipping it in water, caustic soda, or nitric acid, whether hot or cold. Sulphuric or hydrochloric acid has the power of rapidly destroying the intensity of the radiation in a few minutes. A copper-sulphate solution, if only slightly acid, does not act on the wire rapidly. The following example of a test shows the effect of several of the solutions on a radio-active platinum plate. After each immersion the plate was washed in water and dried over a Bunsen-flame. After exposure of 4 minutes to gradually heated water and 2 minutes to boiling water, the rate of discharge fell from 100 divisions

in 15·5 secs. to 100 divisions in 20 secs. After 5 minutes' boiling in caustic soda, the rate of discharge fell to 100 in 27 secs. After 10 minutes' exposure to strong hot nitric acid, the rate of discharge was cut down to one-half its previous value. Dilute sulphuric acid reduced the rate of discharge to one-half in 10 secs. and one-quarter in 60 secs. Both hydrochloric and sulphuric acids are more powerful in destroying the radioactive power than the other solutions examined. In the case of water and caustic soda, the small diminution of intensity appears to be due as much to the mechanical action of the bubbling as to the chemical action on the surface.

The question now arises, whether the loss of radioactivity of the active plate by immersion in solutions is due to the destruction of the radio-active power of the particles or their removal from the plate to the solution. A fine platinum wire, very strongly active, was placed in a few drops of dilute sulphuric acid for several minutes. The wire lost a large proportion of its radioactivity. The dilute acid was then evaporated down to dryness in a sand-bath, and on examination it was found that the residue on the glass surface was strongly active. We may conclude from this experiment that the radioactivity of the particles is not destroyed, but that they pass into solution, and that on evaporating the solvent the substance still remains.

Some experiments were tried to see whether a plate preserved its radio-active power when a layer of copper was electrolytically deposited upon it. A radio-active platinum wire was made a cathode in a copper-sulphate solution, and a current of about half an ampere passed through for 1 minute. The radioactivity was diminished to about ·7 of its value when tested in the usual way. After washing the wire in water, it was allowed to stand some time in air, and the rate of diminution of the radioactivity observed. The intensity diminished more rapidly at first than for an unacted-on wire; but after 10 hours the rate of diminution became normal. The more rapid decrease at first is probably due to the dilute sulphuric acid which remained in the pores of the copper deposit. When the platinum wire was made the anode in a copper-sulphate solution, the radioactivity rapidly diminished. The action in this case was probably due to the production of sulphuric acid at the surface of the anode by the passage of the current which dissolved the radio-active material on the platinum plate.

*Discussion of the Results.*

Before entering on the question of the cause and nature of induced radioactivity, a brief review may be given of the results obtained :—

(1) All thorium compounds examined produce radioactivity in substances in their neighbourhood, if the bodies are all uncharged. With charged conductors the radioactivity is produced on the — charged body. In strong electric fields, the radioactivity can be concentrated on the surface of thin wires. Thorium oxide is the most active of the thorium compounds in causing radioactivity, but loses its power if it is heated for several hours at a high temperature.

(2) The power of producing radioactivity is closely connected with the presence of the "emanation" from thorium compounds, and is in some way dependent upon it.

(3) The radiation excited in bodies is homogeneous, and of a more penetrating character than the radiations from thorium or uranium. The radiation is confined to the surface of the substance, and is independent of whether the substance is a conductor or non-conductor and of the nature of its surface.

(4) The intensity of the radiation emitted falls off in a geometrical progression with the time, decreasing to half its value in about 11 hours. The decay of intensity is independent of the state of concentration of the radioactivity or the nature of the substance.

(5) The amount of induced radioactivity increases at first nearly proportional to the time of exposure, but soon tends to a value when the intensity of the radiation varies very little with increase of the time of exposure.

(6) The amount of induced radioactivity produced in a given time on a conductor depends on the potential-difference between the electrodes, and tends to a constant value for large E.M.F.'s.

(7) The amount of radioactivity is independent of the pressure of the gas, except at low pressures when the amount on the — charged conductor decreases with the pressure. The amount is not much affected whether the gas is hydrogen, air, or carbonic acid.

(8) No increase of weight has been observed by making a body radio-active. The radiation from a platinum wire is not much altered by placing the wire in a flame, hot or cold water, or nitric acid. Hydrochloric and sulphuric acids rapidly remove the radioactivity from its surface. The solution, when evaporated, leaves the active portion behind.

Three possible explanations of the phenomena of induced

radioactivity naturally present themselves :—(a) That the radioactivity is due to a kind of phosphorescence excited in the substance by the radiation from thorium; (b) or to the deposition of the + gaseous ions produced in the gas by the “emanation”; (c) or to the deposition of particles of a radio-active material emitted by thorium compounds.

The hypothesis that the radiation is a kind of phosphorescence will not explain the results observed, since substances are made radio-active outside the incidence of the radiation, and the radioactivity can be concentrated on the — electrode. The question as to whether the induced radioactivity is due to the deposition of a foreign substance on bodies, or to the action of the + ions produced in the gas, or a combination of both, is difficult to decide with certainty from the experimental evidence. The theory that the + ions produced by the emanation are responsible for the radioactivity, at first sight seems to explain many of the results. Since the radio-active particles of the emanation are very small, the intensity of the radiation must be very great near them ; and in consequence of this, ions may not only be produced, but the charges on the ions set in violent vibration: these + ions would be carried to the negative electrode, and gradually dissipate the energy of their vibration by radiation into space. On this theory, however, it is difficult to explain the variation of radioactivity with pressure. At low pressures, the experiments show that the total radioactivity produced is much the same as at atmospheric pressure, but the — electrode receives only a small proportion of the radio-active particles. On the theory that the radio-active particles are + ions, we should expect them in a strong field to be all carried to the — electrode. Another experiment on the variation of the amount of radioactivity with distance also does not fall in readily with this view. The amount of radioactivity was found to be practically the same whether the distance from the radio-active surface was 3 mms. or 3 cms. In the latter case, the number of + ions produced by the emanation is much greater than in the former; but the amount of radioactivity is unaffected.

The theory that the radioactivity is due to a deposition of radio-active particles from the thorium compounds affords a general explanation of all the results ; but the difficulty is to advance a satisfactory reason for the particles obtaining the + charge which they must possess in order to be moved to the — electrode in an electric field. If we suppose the radio-active particles from thorium compounds emitted at a uniform rate, independent of the nature and pressure of the gas, we should

expect to obtain the same total amount of radioactivity spread over a vessel due to diffusion of the particles, as can be obtained by concentration of all the radio-active particles on the — electrode; and the amount should be independent of the pressure and nature of the gas, provided it does not act on the thorium. Some experiments seem to point to the conclusion that the radio-active particles are not charged till they diffuse out into the gas, but that they gain a + charge in the course of time. A possible explanation is that the + charge is obtained by the diffusion of the ions to the surface of the particles. Since there is reason to believe that the — ions in most cases move faster than the + ions in an electric field, there is always an excess of + ions in the gas, and the particles in the gas thus tend to become positively charged. On this supposition, the diminution of the amount of radioactivity on the — electrode at low pressures is due to the fact that there is not a sufficient number of ions in the gas to charge the particles, which thus diffuse to the sides of the vessel.

As far as experiments have gone, the power of exciting radioactivity appears to be confined to thorium compounds. Neither uranium nor radium nor polonium has so far shown any trace of action; but the specimens \* of radium and polonium used were not very radio-active and contained considerable amounts of impurity. A plate made radio-active is not able to excite any appreciable radioactivity in another plate near it. I have tested the + and — electrodes after the passage for several hours of a strong current between them due to Röntgen rays, flames, and discharge from points, but no trace of radioactivity on them has been observed.

Macdonald Physics Building,  
McGill University, Montreal,  
Nov. 22nd, 1899.

\* As this paper was passing through the press the *Comptes Rendus* of Nov. 6th was received, which contains a paper by Curie and a note by Becquerel on the radiation excited in bodies by radium and polonium. Curie has used specimens of these substances 10,000 to 50,000 times more radio-active than uranium and the phenomena observed are, in some respects, similar to those exhibited by thorium compounds; but there are not sufficient data on which to base any comparison. No mention is made of the effect of an electric field, or whether there is an "emanation" from radium and polonium, as there is from thorium compounds. Curie concludes that the results obtained are due to a kind of phosphorescence excited by the radiation; while in the case of thorium the author has shown that such a theory is inadmissible. Further experiments on the comparison of the radioactivity produced by thorium with that produced by radium and polonium will be of interest.

XII. *On the Elasticity of Wires.* By G. F. C. SEARLE, M.A.  
*Demonstrator in Experimental Physics at the Cavendish  
 Laboratory, Cambridge\**.

MR. L. R. WILBERFORCE†, following a suggestion due to Profs. Ayrton and Perry ‡, has described a method of using a spiral spring in the determination of the Young's modulus and the simple rigidity for the material of the wire forming the spring. The great improvement introduced by Mr. Wilberforce consisted in determining the periodic times of the longitudinal and angular vibrations of a mass hung at the end of the spring, instead of measuring the longitudinal and the angular displacements of the end of the spring due respectively to a measured force and a measured couple. Some inquiries from my pupils as to the theory of the method led me to endeavour to simplify the conditions of the experiment, while retaining the principles laid down by Mr. Wilberforce. The apparatus and the method described in this paper are the outcome of that endeavour.

It should be noted at the outset that the assumption is made, in accordance with general practice, that the wires under test may be regarded as formed of isotropic metal. But it is very unlikely that it is possible to produce such a wire except by cutting it out of a very large block of the metal. The results given below show that in some cases isotropy must be very largely departed from; and in fact the method described in this paper may be more valuable in giving an indication of the extent of æolotropy than in giving values of so-called "elastic constants."

I have modified Mr. Wilberforce's method by the substitution of a straight wire for a helical wire, and thus not only is mathematical simplicity gained, but the determination of the radius and the slope of the helix is avoided. Since the wire under test need not be more than a few centimetres long, there is great economy of material; and since the wire is straight, the method is available for materials which may be too brittle to be formed into a helix.

In fig. 1, A B, C D are two equal brass bars of square section. Through the centres of these bars at G, G' holes are drilled, and by means of the clamping arrangement, of which a section is shown in detail in fig. 2, the wire under test is clamped securely to the two bars. By means of two hooks screwed into the bars at G, G' into the faces perpendicular to

\* Communicated by the Author.

† Phil. Mag. Oct. 1894.

‡ Proc. Roy. Soc. vol. xxxvi. p. 311.

those pierced by the holes for the clamping-screws, the system can be suspended by two parallel strings (about 1 metre in length), the plane A B D C being horizontal. The fact that the ends of the hooks, which engage in the strings, are about 4 cm. above the centres of gravity of the bars, ensures that the horizontal position of the plane A B D C is thoroughly stable.

Fig. 1.

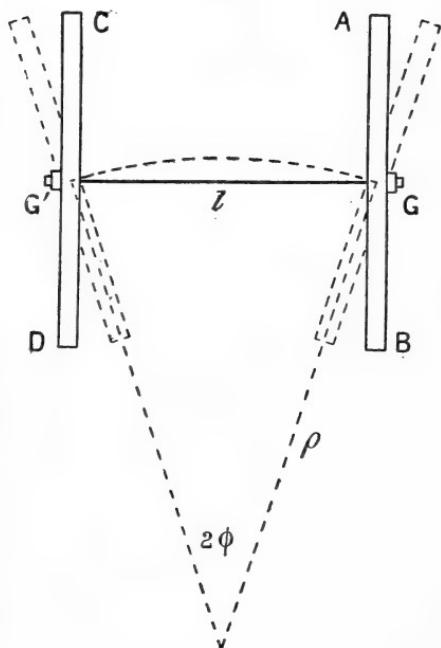
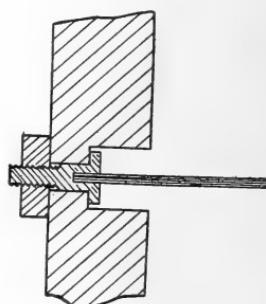


Fig. 2.



If now the two ends B, D are made to approach each other, the displacements of the two bars being equal, and if the bars are then set free, the system will vibrate, each bar executing harmonic vibrations in a horizontal plane. To the first order of small quantities G and G' have no motion along the line joining them; and when there is the additional limitation that the mass of the wire is small compared with that of the bars, the motion of G and G' at right angles to G G' may be neglected. Thus to this order of accuracy the centres of gravity of the bars are at rest, and consequently the action of the wire on either bar is a pure couple. The stress across any section of the wire is a couple of equal value, and thus the wire is bent into a circular arc.

If  $\rho$  be the radius of the arc, the bending-moment is  $EI/\rho^*$ ,

\* Minchin, 'Treatise on Statics,' ed. 3, vol. ii, p. 424.

where  $E$  is Young's modulus, and  $I$  the "moment of inertia" of the area of cross-section of the wire about an axis through its centre of gravity perpendicular to the plane of the arc. Also, if  $\phi$  be the angle turned through by either bar from its equilibrium position, we have  $\rho = l/2\phi$ , where  $l$  is the length of the wire.

If  $K$  be the moment of inertia of either bar about a vertical axis through its centre of gravity, we have for the motion of either bar

$$K \frac{d^2\phi}{dt^2} = -\frac{EI}{\rho} = -\frac{2EI}{l} \cdot \phi. \quad \dots \quad (1)$$

Hence, if  $t_1$  be the time of vibration,

$$t_1 = 2\pi \sqrt{\frac{Kl}{2EI}} \quad \dots \quad (2)$$

When the wire is of circular section with radius  $a$ ,  $I = \frac{1}{4}\pi a^4$ . In this case we find on substitution in (2)

$$E = \frac{8\pi Kl}{t_1^2 a^4}. \quad \dots \quad (3)$$

If now we unhook the bars from the strings and clamp one to a shelf or other suitable support so that the wire  $G'G'$  is vertical, and then cause the other bar to vibrate about a vertical axis, we can determine the simple rigidity. For if  $n$  be the rigidity, the couple required to give to one end of a wire of length  $l$  and radius  $a$  one radian of twist relative to the other end is  $\pi n a^4 / 2l$ \*. Hence the couple experienced by the bar when turned through an angle  $\theta$  is  $\pi n a^4 \theta / 2l$ , and the time of vibration of the bar is

$$t_2 = 2\pi \sqrt{\frac{2Kl}{\pi n a^4}}; \quad \dots \quad (4)$$

so that

$$n = \frac{8\pi Kl}{t_2^2 a^4}. \quad \dots \quad (5)$$

The value of  $K$  in (5) is the same as that in (3), since the bars are square in section, provided either that the hooks are light or that they are removed for this experiment.

We are thus able to compare  $E$  and  $n$  by the simple comparison of the squares of the periods of vibration, for we have

$$\frac{E}{n} = \frac{t_2^2}{t_1^2}. \quad \dots \quad (6)$$

\* Stewart and Gee, 'Practical Physics,' vol. ii. p. 169.

When the material is isotropic, Poisson's ratio, viz. lateral contraction/longitudinal extension, is easily found by the formula

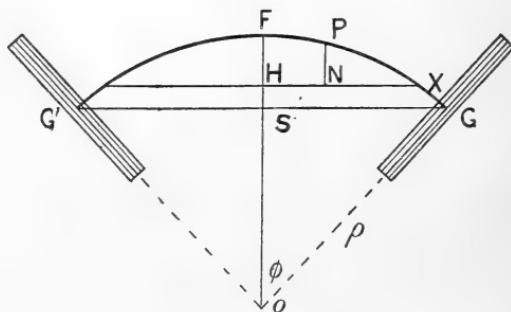
$$\sigma = \frac{E}{2n} - 1. \dots \dots \quad (7)^*$$

Two points remain to be noticed in connexion with the determination of  $E$ . The wire will not generally be absolutely straight. But it is easily shown that small initial curvature (not necessarily uniform) in the horizontal plane is without influence upon the time of vibration. Curvature in a vertical plane calls the rigidity of the material into play; but the effect upon the time of vibration will be small when the wire is nearly straight.

The second point refers to the correction due to the finite mass of the wire. The processes of the theory of the transverse vibrations of rods enable the period to be calculated to any desired accuracy; but a close approximation can be obtained by a very simple method. The process turns upon calculating the kinetic energy of the system on the assumption that for a given angle between the bars the form of the wire, *when in motion*, is the same as its form *when at rest* †.

In fig. 3 let  $F$  be the middle of the wire,  $H$  the centre of gravity of the whole system. Then, provided that the suspending strings are very long,  $H$  is fixed in space, and we

Fig. 3.



may use it as a fixed point to which to refer the velocities of the parts of the system. Let  $S$  be the centre of gravity of the two bars. Let  $M$  be the mass of each bar, and  $m$  the mass of the wire. Let  $P$  be any point on the wire, and let  $PN=y$ ,  $NH=x$ ,  $SH=z$ . Since  $H$  is the centre of gravity

\* Stewart and Gee, 'Practical Physics,' vol. ii. p. 175.

† Lord Rayleigh, 'Theory of Sound,' ed. 2, vol. i. § 88.

of the system, we find, as far as  $\phi^2$ ,

$$FH = \frac{M + \frac{1}{6}m}{M + \frac{1}{2}m} \cdot \frac{1}{2}\rho\phi^2 = \frac{M + \frac{1}{6}m}{M + \frac{1}{2}m} \cdot \frac{1}{4}l\phi;$$

and hence

$$y = \left( \frac{M + \frac{1}{6}m}{M + \frac{1}{2}m} - \frac{4x^2}{l^2} \right) \frac{1}{4}l\phi.$$

Also

$$z = \frac{\frac{1}{3}m}{M + \frac{1}{2}m} \cdot \frac{1}{4}l\phi.$$

Hence, if  $T$  be the kinetic energy, we have

$$T = 2 \left[ \frac{1}{2} K\dot{\phi}^2 + \frac{1}{2} M\dot{z}^2 + \int_0^{\frac{l}{2}} \frac{1}{2} \frac{m}{l} \dot{y}^2 dx \right].$$

Effecting the integration and reducing, we find

$$T = \frac{1}{2} \dot{\phi}^2 \times 2 \left( K + \frac{ml^2}{60} \cdot \frac{M + \frac{1}{12}m}{M + \frac{1}{2}m} \right). \quad \dots \quad (8)$$

For the potential energy we have

$$V = \frac{1}{2} \phi^2 \cdot \frac{4EI}{l}; \quad \dots \quad (9)$$

and thus

$$t_1 = 2\pi \sqrt{\frac{K + \frac{ml^2}{60} (M + \frac{1}{12}m)/(M + \frac{1}{2}m)}{2EI/l}}. \quad \dots \quad (10)$$

Hence with sufficient accuracy

$$E = \frac{8\pi K l}{t_1^2 a^4} (1 + ml^2/60K). \quad \dots \quad (11)$$

Some practical details may be added. In the first experiment (for finding  $E$ ), in order to set the bars into vibration without giving them any motion of translation, it is convenient slightly to draw together the two ends  $B$ ,  $D$  by a loop of cotton-thread. The system, thus constrained, is then brought to rest, and the desired vibration is started by burning the thread.

The motion of the bars must be small in order that the most highly strained portions of the wire may not be strained beyond the elastic limit. I have found that when the arc of vibration is large, there is rapid damping even with "silver"-steel wire, while at the same time the time of vibration is greater than for small arcs. But when the vibration has become

sufficiently small the damping becomes very small, indicating that the elastic limit is not overstepped. With a steel wire 31·4 cms. in length and .0698 cm. in radius, I find it easy to count 100 vibrations of one of the bars with an initial deflexion of not more than 1°, the elasticity being practically perfect. This result might be expected, for in this case the greatest stress experienced by any part of the wire is only about  $\frac{1}{100}$  of the breaking stress.

The suspending strings must be long and fine, so that the torsional couples due to them may be negligible.

Since any departure from the circular form of section of the wire has an important influence upon the time of vibration in the determination of E, it is advisable to mark one of the clamping-screws, and to take two sets of observations for the period with the mark (1) vertical, (2) horizontal. The mean of the two values is to be used in the formulæ (3) or (11). The two corresponding diameters should be measured by a screw-gauge and the mean taken, or the mean diameter should be found by the hydrostatic balance.

The form of clamping-screw shown in fig. 2 is convenient; for if a number of wires of various metals are provided with clamping-screws, the same inertia-bars serve for all the wires. If short wires are used, the clamping-screws should be recessed into the bars so that the end of the screw may be in the centre of the bar, as shown in fig. 2 \*. The wires are soldered into holes drilled into the screws.

The only remarks necessary with regard to the determination of the rigidity are that small arcs of vibration should be used, and that the suspending-hooks should be so light that their moments of inertia about the axis of the wire are negligible.

The masses of the bars should be determined, and, for convenience, marked upon the bars *before* the holes are drilled in them.

The dimensions of my apparatus are as follows:—

Length of each bar = 32·1 cms.

Width of each bar (square in section) = 1·25 cm.

Mass of each bar = 441 grammes.

Moment of inertia of each bar =  $3\cdot793 \times 10^4$  grm. cm.<sup>2</sup>

Length of wires under test = 31·4 cms.

Diameter of wires tested = ·1 to ·15 cm.

The following are some of the results obtained, the unit for each modulus being one dyne per square centimetre. In each case the value of E has been corrected for the mass of

\* This is not the case in my apparatus; the end of the screw is about ·6 cm. from the centre of the bar.

the wire, the correction amounting to about  $\frac{1}{10}$  per cent. in the value of E.

	E.	n.	E/n.	$\sigma$ .
" Silver "-steel .....	$1.981 \times 10^{12}$	$7.872 \times 10^{11}$	2.516	.258
Brass (hard-drawn) .....	1.022	3.715	2.751	.376
Phosphor-bronze .....	1.201	4.359	2.755	.378
Silver (hard-drawn) .....	.778	2.816	2.762	.381
Copper (hardened by stretching) ..	1.240	3.880	3.195	.598
Copper (annealed) .....	1.292	4.018	3.217	.608
Nickel (hardened by stretching) ...	2.395	7.424	3.227	.614
Platinoid .....	1.359	3.602	3.773	.887
German-silver (hard-drawn) .....	1.155	2.618	4.414	1.207

For the last four substances  $E/n$  is greater than 3, and consequently  $\sigma$  is greater than  $\frac{1}{2}$ . If the material were isotropic, this would imply that the bulk-modulus is negative, or, in other words, that a hydrostatic pressure applied to the material would result in an increase of bulk. The inference is that wires of these four substances are so far from being isotropic that it is improper to apply the theory of isotropic solids to them.

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### XIII. *Photometry of the Diffuse Reflexion of Light on Matt Surfaces.* By HENRY ROBERT WRIGHT, Ph.D.\*

#### HISTORICAL INTRODUCTION.

L AMBERT'S † law ( $q = \Gamma_1 ds \cos i \cos \epsilon$ ), which is known under the name of the law of the cosine, has been shown especially by Seeliger's ‡ investigations not to be rigidly true, but only approximately so in a very few cases. No theoretical proof has so far been adduced and the experiments made by Bouguer §, Kononowitsch ||, Seeliger,

\* Communicated by the Author; published also in Wied. *Ann. vierte Folge*, Bd. i. p. 17, 1900.

† J. H. Lambert, 'Photometria sive de mensura et gradibus luminis colorum et umbrae', Augsburg, 1760.

‡ Seeliger, *Vierteljahrsschr. der Astr. Gesellsch.* xx. Heft 4, p. 267, 1885, and xxi. Heft 3, p. 216, 1886, and *Sitzungsber. der math.-phys. Classe der königl. bayr. Acad. d. Wissenschaften* Heft 2, p. 201, 1888.

§ Bouguer, 'Histoire de l'Académie Royale des sciences.' Paris, 1757 (1762), and 'Traité d'optique sur la gradation de la lumière. Ouvrage posthume de M. Bouguer, et publié par M. l'Abbé de Lacaille': Paris, 1760.

|| A. Kononowitsch, *Schriften der math. Abth. der Neurussischen naturforsch. Gesellsch.* t. ii.; *Fortschr. d. Physik*, xxxv. p. 430, 1879, and *Schriften der neu russ. (Kiew) Univ.* xxii. 107; *Fortschrifte der Physik*, xxxvii. 2, p. 481, 1881.

Messerschmitt \*, and Chwolson † also show great deviations. The results of Wiener ‡ and in one particular case of Seeliger conform in the main to it. Lommel §-Seeliger's law

$$\left( \text{simplest form } L = \Gamma_2 \cdot ds \cdot \frac{\cos i \cos \epsilon}{\cos i + \cos \epsilon} \right)$$

shows deviations from the results of direct observation which are at least as considerable as are those from Lambert's law. In this connexion, the observations on the radiation of heat are worthy of notice, as they are based on very sensitive objective methods. Provostaye and Desains ||, Maquenne ¶, Godard \*\*, and Hutchins †† confirm for small angles of incidence the law of the cosine without any exception. Ångström ‡‡ alone found empirically Lommel's law, but this conclusion was due to a fundamental error in the disposition of his experiments, as he himself admits in a later publication. A closer examination of the above-mentioned results does not warrant the conclusions to the extent drawn by the investigators. They only show that no absolutely matt surfaces are found in nature, and that therefore the law of the cosine is not valid for natural bodies, more particularly in the case of the stars. Seeliger's experiments were made specially for astronomo-photometric purposes, and it is hence impossible to draw strict deductions from them which shall apply to really matt surfaces. Messerschmitt, on the other hand, committed errors in principle, which will subsequently be referred to; whilst Kononowitsch used a substance so unsuitable that his results cannot be taken into consideration. It was hence necessary to obtain new results, which should be based strictly on the grounds which the theory demands.

\* J. B. Messerschmitt, Wied. *Ann.* xxxiv. p. 867, 1888.

† O. Chwolson, *Mélanges phys. et chim. tirés du Bull. de St. Pétersbourg*, xii. p. 475-545 und Beibl. xi. p. 149, 1887.

‡ Chr. Wiener, Wied. *Ann.* xlvi. p. 638, 1892.

§ E. v. Lommel, Wied. *Ann.* x. p. 449, 1880; *Sitzungsber. der math. phys. Classe d. königl. bayr. Acad. d. Wissenschaften zu München*, p. 95, 1887; and Wied. *Ann.* xxxvi. p. 473, 1889.

|| F. de la Provostaye et P. Desains, *Comptes Rendus*, xxiv. p. 60, 1847; *Pogg. Ann.* lxxiv. p. 147, 1849; *Compt. Rendus*, xxxiii. p. 444, 1851; *Ann. chim. et phys.* (3) xxxiv. p. 192, 1852.

¶ Maquenne, Thèses présentées à la Faculté des Sciences de Paris, 1880.

\*\* L. Godard, *Ann. chim. et phys.* (6) x. p. 354, 1887, and *Journal de Physique*, (2) vii. p. 435, 1888.

†† C. C. Hutchins, *American Journal of Science*, November 1898.

‡‡ Knut Ångström, Wied. *Ann.* xxvi. p. 253, 1885, and *Bihang till k. Svensk. vet. Ak. Handl.* xiii. Afd. I. Nr. 4, p. 12, 1887, and *Beibl.* xii. p. 197, 1888.

## I. EXPERIMENTAL PART.

*Preparing the Plates.*—Powders loosely sifted and having a level surface would undoubtedly answer the postulate of the theory best. This would, however, necessitate a *horizontal* position of the surfaces, which renders the investigations very laborious. It is therefore advisable to have the substances in the shape of plane plates, so that the surface to be experimented upon can be brought into a vertical position. Cements such as gum &c. have been shown to change the optical properties of the powders in a high degree. Casting (plaster of Paris) also causes more or less *normal* reflexion, which must by all means be avoided. The best method, as I have found, is to compress the powders by means of an hydraulic press and a steel stamping-iron. With suitable support at the base and a pressure of from 4 to 20 tons, the necessary solidity for delicate treatment is obtained. No normal reflexion can be detected on the plates, as the following results will show; even the size of the powdery particles is not changed. Thus the chief source of such errors as all investigators have hitherto fallen into is fully avoided.

*The Polarization of the Scattered Light* had to be dealt with first in order to decide whether a polarization-photometer could be used. In contrast to media with very small suspended particles such as solutions of colloids &c., the scattered light reflected by powders is *not polarized*, as Provostaye and Desains\* have shown. The linear dimensions compared with the length of the reflected waves are in the first case of the same order or even smaller than the waves, whilst the powder particles have an average diameter of 0·002 mm. The size is evidently of the same importance here as it is in respect to the colour (Rayleigh's theory) of the light of the sky. The above-mentioned plates have been studied with a "Haidinger'sche Lupe" and no polarization was found; even polarized incident light was reflected depolarized (with exception of the limit angles  $\epsilon = 80^\circ$  and  $i = 60^\circ$  or  $80^\circ$ ). This shows the perfection of the plates and permits the employment of a polarization-photometer, to the use of which Messerschmitt was not entitled as his substances polarized the light.

*The Disposition of the Experiments* must be such that parallel light can fall under any angle of incidence ( $i$ ) on the surface of the substance, and that the reflected scattered light can be observed under any angle of emission ( $\epsilon$ ) by the

\* F. de la Provostaye et P. Desains, *Ann. chim. et phys.* (3) xxxiv, pp. 196, 216 (1852).

photometer. The plate (*a*) (see figure) is fixed with the surface in a vertical plane on the table (*b*), which turns round a vertical axis and carries a graduated circle (*c*). The source of light has a fixed position and is not to be moved; the angle of incidence is varied by turning the table (*b*). The graduated circle (*d*) concentric to (*c*) determines the angle of emission. Contrary to other investigations in this line only *one* source of light has been used instead of two. The advantage of this method is self-evident inasmuch as all variations of the intensity are eliminated.

*The Standard of Comparison* is drawn from the source of light which illuminates the plate in the following way:—A mirror (*f*) placed at  $45^\circ$  to the horizon, the centre of which is in the vertical axis of the graduated circle, throws the parallel horizontal rays of light vertically down upon a diffuse reflecting plate (*a'*). This little plate, of the same substance as the one which is to be studied, is inclined at nearly  $45^\circ$  and projects the light scattered to the slit of the photometer. At the commencement the size and angle can be suitably varied between certain limits so that one is able to gain very nearly the same intensity of the standard of comparison as the plate itself has. This, of course, makes the measurements more exact.

*The Source of Light* is an arc-lamp of about 500 candle-power, which burned with great constancy after having been carefully regulated. This was chosen as the best means of procuring a parallel beam of light of great intensity, such as the theory demands.

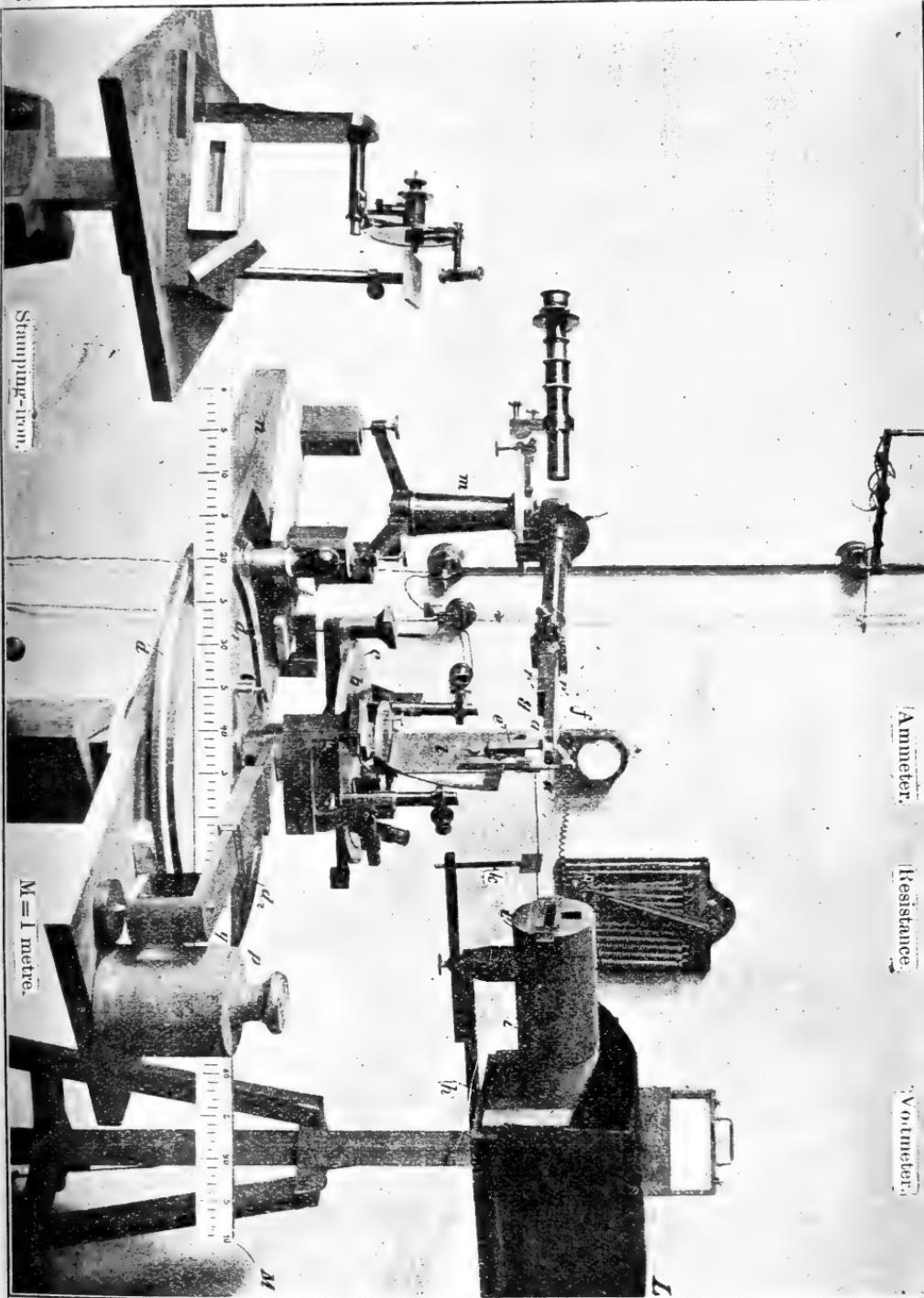
As *Photometer* Glan's \* spectrophotometer was used. In front of the slit I placed Crova's † little plate with convergent edges. The width of the slit was only 0·4 mm. To be prepared for all eventualities the Wollaston prism was turned so that light with a vertical plane of polarization entering the lower half of the slit vanishes; because the traces of reflected polarized light vibrate in a vertical plane when at all visible.

*The Selection of the Parallel Rays out of the Scattered Light.*—The theory demands not only for the incident rays but also for the reflected ones that they should be parallel; not conical as was markedly the case with other observers. As each particle scatters light in all directions, we have to separate one of these rays from the others and to prevent the latter from reaching the photometer. For this purpose it is best to make use of a cylinder-lens (*g*) placed at its focal distance

\* P. Glan, 'Ueber ein neues Photometer,' *Wied. Ann.* i. p. 351 (1877).

† M. A. Crova, *Ann. chim. et. phys.* (5) xix. p. 495 (1880).

Apparatus for observing the polarization.



both from the slit and from the diffuse reflecting plate. All rays parallel to the optical axis of the collimator unite in one straight line, which coincides with the slit, whilst all other rays fall either to the right or to the left of it on to the carefully blackened metal parts of the photometer, and cannot possibly reach the eye. The selection of the focal distance and the size of the lens are very important for the results.

*The Adjustment of the Apparatus.*—The arc-lamp (compare figure) rests on a stand, which can be raised and lowered by means of a cog-wheel. It is also movable in two directions in a horizontal plane. A Zeiss condensing-lens spherically corrected procures the parallel beam of light. A circular hole (*h*) is cut in the box carrying the condensing-lens so that the centre of it lies in its optical axis. It is used as a stop and also for centering the arc of the lamp. The closed end of the cardboard tube (*i*) contains three apertures, which are of such dimensions that only the plates were illuminated. To make the border of the dark parts of the instrument more exact still, the movable screen (*k*) was used. The diffuse reflecting plate (*a*) was gently pressed by two brackets, fixed with springs, against the brass piece (*l*), which could be levelled by means of three adjusting-screws. It stood on a "Meyerstein" spectrometer, from which the collimator and telescope were removed. The graduated circle (*c*) with two verniers is read by means of the two microscopes. The photometer rests on a sliding board, which is carried by the part (*n*). A weight of 10 kg. balances the whole, which turns round the same axis as the plate (*a*). The angles are read by the large graduated circle (*d*) (diameter 51 cm.) and the dials (*d*<sub>1</sub>) and (*d*<sub>2</sub>). The directions of the condensing-lens-, cylinder-lens-, and collimator-axes must of course meet in the axis of rotation, which must also pass through the centre of the little plate (*a'*), the mirror (*f*), and must lie in the surface of the plate (*a*). A specially contrived body (*r*), made of tin, prevents any extraneous light from coming into the photometer, and carries the above mentioned cylinder-lens (*g*) and plate (*a'*). The slit (*i'*) sends light on to a small mirror whose surface lies in the axis of rotation and which is fixed on the brass piece (*l*). Thus one is enabled to observe whether the angle between the incident ray and the zero of the graduated circle is actually 90°.

*The Photometric Measurements.*—Two different methods are at our disposal :

*1st Method.*—The length of the plate with regard to the dimensions of the photometer is *constant*. Or : the projection

on a plane perpendicular to the observed ray decreases with increasing angle  $\epsilon$  as the cosine of this very angle  $\epsilon$ .

*2nd Method.*—The length of the part of the plate which is observed is *not constant*, but increases with increasing angle  $\epsilon$  as the cosine of  $\epsilon$ . Or : the projection on a plane perpendicular to the observed direction is *constant*.

In case of homogeneous illumination the results of the second method multiplied by  $\cos \epsilon$  are the same as by the first method. The reasons for using the second more complicated method will easily be seen from the following:—For the sake of simplicity let us suppose Lambert's law is true. Then the first method will yield for  $i=0^\circ$  and  $\epsilon=0^\circ$ , the intensity of the reflected light  $L=1000$ ; for  $\epsilon=80^\circ$ ,  $L=173$ . Such enormous differences cannot be measured with exactitude by any existing photometer. The second method, on the other hand, will yield for the same angles  $\epsilon=0^\circ$ ,  $L=1000$ , and  $\epsilon=80^\circ$ , also  $L=1000$ . By multiplying with  $\cos \epsilon$  we get, of course,  $L=1000$  and  $L=173$ , as before. Now, if Lambert's law is not strictly correct, we still are forced to admit the superiority of the second method. A further advantage is the exact knowledge of the extent of the deviation, whilst by method I. it may very easily occur that when the angles of emission are small one involuntarily uses method II. without noticing it. According to the results of Messerschmitt there is little doubt that this mistake was made by him. The values of the intensity of the reflected light are nearly constant between  $\epsilon=20^\circ$  and  $60^\circ$ , and they begin then suddenly to decrease very rapidly. By using method I. it is evident that a certain limit length of the plate may by no means be exceeded, whilst by the second method the minimum dimensions may be exceeded to any extent. Naturally this fact is made use of in the experiments so as to be certain that no errors due to size can occur.

It may be interesting to mention that Lambert elaborated his famous law by means of method II. He noticed that a whitewashed wall looks equally bright from any angle ( $\epsilon$ ) when the sun is shining on it.

It is superfluous to say that the observations were made in an absolutely dark room, with the head under a black cloth, and that every possible precaution was taken. The measurements were made in the first and third quadrant of the nicol, which, according to Bakhuyzen\*, is absolutely sufficient. As far as possible the angles of emission ( $\epsilon$ ) were observed on both sides of the plate-normal. For coloured

\* H. G. van de Sande Bakhuyzen, Pogg. Ann. cxlv. p. 259 (1872).

substances that wave-length ( $\lambda$ ) was used which seemed most brilliant in the spectrum. Wrong results may ensue from an imperfectly homogeneous illumination of the surface. To eliminate this I measured after each observation the starting-point, and abandoned results which differed more than 5 per cent. If less than 5 per cent. the geometrical mean of the two values was used as a reference.

*The Compensation of the Measurements.*—The measured quantities are not the real objective-intensities of illumination; they are only functions of them, being the excitation produced on the eye. According to Fechner's psycho-physical law the intensity of the sensation is proportional to the logarithm of the excitation. Consequently these logarithms must be used for the compensation. Gauss's law of the least squares leads to the following formula for the most probable value  $\chi$  when by the different measurements for the same intensity the values  $h_1, h_2 \dots h_n$  are found,

$$\log \chi = \frac{\log h_1 + \log h_2 + \dots + \log h_n}{n}.$$

The following tables have been calculated in this way, using 4, 6, or 8 single readings, and are given in the logarithms themselves. The characteristic has been omitted as being superfluous.

### THE RESULTS.

#### (1) English Red ( $F_2O_3$ ): $\lambda = 612 \mu\mu$ .

$\epsilon$ .	$i=0^\circ$ .	$i=20^\circ$ .	$i=40^\circ$ .	$i=60^\circ$ .	$i=80^\circ$ .
-50°	...	...	...	...	1888
-40	...	...	...	...	1838
-30	...	...	...	6710	
-20	...	...	...	6931	2592
-10	...	...	8861		
0	...	...	8838	7294	2978
+10	...	9734			
+20	...	9508	8532	6955	2650
+30	9357				
+40	8788	8562	7630	6109	1762
+60	6894	6750	6123	4283	6156
+80	2397	2203	2044	9133	1435

(2) Chromate of Potash ( $K_2CrO_4$ ) (yellow) :  $\lambda = 589 \mu\mu.$ 

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	0824
-40	...	...	...	...	1510
-30	...	...	...	6672	
-20	...	...	...	69 7	2572
-10	...	...	8948		
0	...	...	9002	7212	2723
+10	...	9600			
+20	...	9423	8704	6995	2420
+30	9375				
+40	8744	8440	7817	6426	1892
+60	6947	6673	6004	5036	0830
+80	2424	2186	1398	1404	1017

(3) Zinc or Rinmann's Green :  $\lambda = 535 \mu\mu.$ 

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	1460
-40	...	...	...	...	1138
-30	...	...	...	6384	
-20	...	...	...	6687	1992
-10	...	...	8647		
0	...	...	8712	6958	2263
+10	...	9111			
+20	...	8920	8462	6694	1992
+30	9375				
+40	8850	8048	7554	5833	1573
+60	6997	6130	5949	4808	2362
+80	2382	1445	1785	1971	2360

(4) Ultramarine Blue :  $\lambda = \text{Mixed waves.}$ 

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	1030
-40	...	...	...	...	1780
-30	...	...	...	6277	
-20	...	...	...	6675	2667
-10	...	...	8544		
0	...	...	8726	6676	2750
+10	...	9576			
+20	...	9121	8470	6737	3042
+30	9375	...			
+40	8947	8703	7729	5761	
+60	6961	7169	6943		
+80	1968	1851	0951		

(5) Carbonate of Magnesia:  $\lambda = 656 \mu\mu$ .

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	9812
-40	...	...	...	...	0547
-30	...	...	...	6148	
-20	...	...	...	6700	1434
-10	...	...	8394		
0	...	...	8488	6843	1650
+10	...	9437			
+20	...	9317	8243	6700	1546
+30	9375	...			
+40	8757	8458	7491	5838	0874
+60	6792	6465	5558	4655	1007
+80	2115	1872	0884	1173	0592

(6) Carbonate of Magnesia:  $\lambda = 492 \mu\mu$ .

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	9399
-40	...	...	...	...	0308
-30	...	...	...	5117	
-20	...	...	...	5548	1020
-10	...	...	8394		
0	...	...	8382	5869	1262
+10	...	9294			
+20	...	9145	8137	5598	1221
+30	9375				
+40	8870	8120	7277	4685	0476
+60	6932	6267	5319	3718	0702
+80	2311	1702	0752	0175	9853

(7) Carbonate of Magnesia:  $\lambda = \text{Mixed waves}$ .

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	9226
-40	...	...	...	...	9988
-30	...	...	...	5197	
-20	...	...	...	5551	0875
-10	...	...	8065		
0	...	...	8131	5821	1145
+10	...	9400			
+20	...	9196	7861	5551	0875
+30	9375				
+40	8842	8309	6939	4964	9988
+60	6989	6456	5121	6344	1205
+80	2396	1863	1134	2618	0395

## (7 a) Mean Values of Nos. 5 and 6 for Carbonate of Magnesia.

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	9605
-40	...	...	...	...	0427
-30	...	...	...	5782	
-20	...	...	...	6124	1227
-10	...	...	8394		
0	...	...	8435	6356	1456
+10	...	9365			
+20	...	9231	8190	6149	1368
+30	9375				
+40	8843	8289	7384	5261	0675
+60	6862	6366	5438	4186	0854
+80	2213	1787	0818	0674	0222

(8) Plaster of Paris :  $\lambda = 656 \mu\mu.$ 

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	0346
-40	...	...	...	...	0975
-30	...	...	...	6674	
-20	...	...	...	6901	1862
-10	...	...	8773		
0	...	...	8789	7197	2133
+10	...	9621			
+20	...	9366	8722	6951	1954
+30	9375				
+40	8763	8582	7708	6165	1158
+60	6989	6652	5880	4616	0814
+80	2396	2136	1262	1060	9733

(9) Plaster of Paris :  $\lambda = 492 \mu\mu.$ 

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	9762
-40	...	...	...	...	0465
-30	...	...	...	6165	
-20	...	...	...	6443	1441
-10	...	...	8531		
0	...	...	8676	6714	1682
+10	...	9317			
+20	...	9061	8354	6469	1499
+30	9375				
+40	8709	8253	7518	5632	0611
+60	6857	6610	5820	3956	0076
+80	2290	1833	1150	0481	9000

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	9487
-40	...	...	...	...	0249
-30	...	...	...	5510	
-20	...	...	...	5864	1136
-10	...	...	8065		
0	...	...	8131	6134	1406
+10	...	9500			
+20	...	9296	7861	5864	1136
+30	9375				
+40	8842	8409	6939	4977	0249
+60	6989	6556	5121	3427	0324
+80	2396	1963	0528	9138	8935

(10 a) Mean values of Nos. 8 and 9 for Plaster of Paris.

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
-50°	...	...	...	...	0054
-40	...	...	...	...	0720
-30	...	...	...	6419	
-20	...	...	...	6672	1651
-10	...	...	8652		
0	...	...	8732	6955	1907
+10	...	9469			
+20	...	9213	8538	6710	1726
+30	9375				
+40	8736	8417	7613	5598	0884
+60	6923	6631	5850	4286	0445
+80	2343	1984	1206	0770	9366

 (11) Mirror :  $\lambda=612 \mu\mu.$ 

$\epsilon.$	$i=0^\circ.$	$i=20^\circ.$	$i=40^\circ.$	$i=60^\circ.$	$i=80^\circ.$
+10°	...	1.8346			
+20	...	...	0.3495		
+30	9.9375	3.0189	2.0965		
+40	...	1.3436	...	0.5352	
+50	...	...	2.9541	2.2278	
+60	...	9.9266	1.3642		
+70	...	...	1.6049	2.7361	

The reference-point in all the above tables is, as is evident,  $i=0^\circ$  and  $\epsilon=30^\circ$ . This has been made equal to the value of Lambert (9.9375) :  $i=\epsilon$  is the position of the regular reflexion, whilst by  $i=-\epsilon$  the two rays would coincide.

*Carbonate of Magnesia*,  $MgCO_3$ , which Jenko \* erroneously

\* Jenko, Wied. Ann. lxvi. p. 1182 (1898).

believes to be the only existing matt substance, was observed at two different places in the spectrum which, according to Helmholtz, 'Physiologische Optik' (p. 317), are complementary colours. The same applies to plaster of Paris. The mixed waves were measured in the same way as with ultramarine by removing the prism of the photometer. The accuracy was only 6 per cent.; but to these last-mentioned measurements no especial importance was attached; they were only made for reasons which will be subsequently shown.

Even the best *mirrors* scatter light, which has been observed by the photometer. From the results it is evident that this scattered light *obeys perfectly different laws* from those of matt substances.

*No regular Reflexion from the Plates.*—The following table gives the absolute differences of the observations from  $+e$  and  $-e$ :

	$i=60,$ $e=20.$	$i=80,$ $e=20.$	$i=80,$ $e=40.$
English red .....	+ 0·0024	+ 0·0058	- 0·0076
Chromate of potash .....	+ ·0028	- 0·152	+ 0·382
Zinc green .....	+ ·0007	0·000	+ 0·435
Carbonate of magnesia. { red part of spectrum .	·0000	+ 0·0082	+ 0·327
blue part of spectrum .	+ ·0050	+ 0·0201	+ 0·168
Plaster of Paris. { red part of spectrum .	+ ·0050	+ 0·0092	+ 0·183
blue part of spectrum .	+ ·0026	+ 0·0058	+ 0·146

Taking even the angle of  $80^\circ$  still into account the mean variation is only 0·121, that is, 2·8 per cent. This being very near (0·8 per cent.) the limits of accuracy of the indications, we must admit that *both* the *light intensities* are the *same*. This is a strong argument for the superiority of my plates.

*Influence of Colour.*—Comparing the results we find that in nearly all cases for a constant  $e$  the values for varying angles  $i$  are greater for red than for yellow, and these again greater than for green. On the other hand the values for  $i =$  constant and  $e$  varying are almost the same for all colours. Hence the colour seems to be of greater influence for the angle of incidence than for the angles of emission. Messerschmitt found the first result also, and tried to explain it by means of Fresnel's observation, that the limit-angle, from which the regular reflexion begins, varies for different

colours. The regular reflexion begins sooner for red than for yellow, green, &c. This fact alone, I believe, can scarcely be a sufficient explanation, because Fresnel \* and Hankel † used angles of  $79^\circ$  as a minimum, whilst here the phenomenon can be noticed already at  $20^\circ$ .

The law for the angle of emission having been found to be independent of the colour, I believe to have proved the truth of von Lommel's hypothesis, that the so-called coefficient of diffusion is independent of the wave-length for particles of the said dimensions. Contrary to this the dependence upon colour has been shown by Christiansen ‡ in the case of very small suspended particles. This cannot, however, be used as an argument against my assertion, because the size of the particles is so very different, and the situation altogether another one; especially as the ratio of the refractive indices is very nearly unity by Christiansen's experiments.

If we compare the mean of the complementary colours (tables 7 a and 10 a) with the values found without the use of a prism, we find deviations which exceed the accuracy of the measurements very much. In the first case we combine the angles ( $\alpha$ ) of the Nicol in the following way :

$$\frac{\tan^2 \alpha_{\text{red}} + \tan^2 \alpha_{\text{green}}}{2}.$$

In the second case we read an angle  $\alpha'$ , of whose relation to the angles for  $\alpha_{\text{red}}$ ,  $\alpha_{\text{green}}$ , &c., we are in total ignorance, as physiological questions arise here. Hence we see theoretically that the values of both tables are probably different, and the experiments confirm this also. Thus one is not able to establish a law for white light, after having made observations of the plate at different parts of the spectrum only. And it is also not permissible to draw an inference from Messerschmitt's results (p. 884). They only show that a deviation exists ; but its value is absolutely unknown.

## PART II.

If the variations between the results and the theory are given, as in the case of other observers, only the law as a whole can be considered. It is, however, a great advantage to compare the single elements of the law with the reality. Hence I append the following tables :

1. *Deviation from the Law of Incidence.*—The figures are

\* A. Fresnel, *Oeuvres complètes*, i. p. 225.

† W. Hankel, Pogg. Ann. c. p. 302 (1857).

‡ C. Christiansen, Wied. Ann. xxiii. & xxiv. 1884 & 1885.

those which would have to be added to  $\log \cos i$  (Lambert) in order to give the real results.

$i.$				In the mean	
	English red.	Chromate of potash.	Zinc green.	Carbonate of magnesia.	Plaster of Paris.
$i = 0^\circ \epsilon = 30^\circ$	0000	0000	0000	0000	0000
$i = 20^\circ \epsilon = 10$	+0071	-0063	-0552	-0298	-0194
$i = 40^\circ \epsilon = 0$	-0004	+0160	-0130	-0407	-0110
$i = 60^\circ \epsilon = 0$	+0205	+0223	-0031	-0633	-0034
$i = 80^\circ \epsilon = 0$	+0582	+0327	-0133	-0940	-0489
Ergo :	$\Theta' = 0240$	$\Theta' = 0193$	$\Theta' = 0211$	$\Theta' = 0569$	$\Theta' = 0207$

2. *Deviations from the Law of Emission.*—The figures would have to be added to  $\log \cos \epsilon$  (Lambert) to give the real results.

$i.$				In the mean	
	English red.	Chromate of potash.	Zinc green.	Carbonate of magnesia.	Plaster of Paris.
$i = 0^\circ$	0050	0056	0010	0113	0075
$i = 20^\circ$	0037	0059	0077	0046	0062
$i = 40^\circ$	0298	0017	0236	0040	0081
$i = 60^\circ$	0032 *	0213 *	0020 *	0064 *	0063 *
$i = 80^\circ$	0057 *	0179 *	0233 *	0280 *	0112 *
	$\Theta'' = 0095$	$\Theta'' = 0105$	$\Theta'' = 0115$	$\Theta'' = 0109$	$\Theta'' = 0079$

\*  $\epsilon = 60^\circ$  and  $\epsilon = 80^\circ$  is omitted in the calculation of  $\Theta''$ .

3. *Deviation from Lambert's law in totality:*

English red.	Chromate of potash.	Zinc green.	Carbonate of magnesia.		Plaster of Paris.	
			Red part of spectrum.	Blue part of spectrum.	Red part of spectrum.	Blue part of spectrum.
$\Theta = 0223$	$\Theta = 0245$	$\Theta = 0255$	$\Theta = 0282$	$\Theta = 0554$	$\Theta = 0132$	$\Theta = 0254$

0 0043 unit of Brigg's logarithms being 1 per cent. of the

intensity of illumination, we find in percentages the following deviations :—

	English red.	Chromate of potash.	Zinc green.	In the mean.	
				Carbonate of magnesia.	Plaster of Paris.
$\Theta$ in p.c.	5·3 p.c.	5·8 p.c.	6·1 p.c.	10·1 p.c.	4·6 p.c.
$\Theta'$ in „	5·7	4·6	5·0	14·0	4·9
$\Theta''$ in „	2·2	2·5	2·7	2·5	1·8

Considering that the probable error in the investigations is 2 per cent. we see from these tables that the *law of the cos i* is not valid. The values of the angles of incidence for constant  $\epsilon$  are in the mean smaller than Lambert's, a result which Seeliger and Wiener have also found. The *law of the cos  $\epsilon$*  is, on the other hand, *perfectly correct*, whilst Lambert's law in totality naturally shows great deviations caused by the  $\cos i$ . Hence a law of illumination can never be symmetrical in reference to  $i$  and  $\epsilon$ .

With respect to the results of other observers it seems somewhat surprising to find the general validity of the law of the  $\cos \epsilon$ . But examining the results more closely one finds that the observations come the nearer to the law of the  $\cos \epsilon$  the more matt the plates were or, what is the same thing, the less normal reflexion they showed. Well, it seems to me at the first start hardly reasonable to expect that plates which reflect the light normally can follow a law which does not take this into account at all; it is clear that the plates must be really matt if one wishes to deduce a theory from observations of them. This makes it plain why I took so much trouble to obtain matt plates from the powders, and the results show that by this method of pressure one is able to get them in the required condition. It is worthy of regard that it has not been possible yet to prove Lambert's law theoretically as Zöllner and Seeliger have shown. But that is in my view no reason why it should not exist. As shown in the beginning, the very sensitive objective observations in the analogous case of radiant heat likewise confirm the law of the  $\cos \epsilon$ , whilst the law of the  $\cos i$  is also found to be not correct.

Hence von Lommel's law is not valid. There are a number

of possibilities which can explain the deviations, and which may be mentioned here :—

1. The law takes only rays into consideration which come from the inside of the plate. Undoubtedly the diffuse reflexion of the surface is so great that it cannot be ignored.

2. The refraction of the incident and reflected rays has been disregarded. There can be no doubt that in reality the rays must be refracted as they pass from one medium into another and different one.

3. von Lommel assumed that the same quantity of light  $l.dv.d\rho$  is diffused in all directions. As regards the front half of the particles (looking on to the plate) the truth of this is fully established by my experiments for azimuths  $0^\circ$  and  $180^\circ$ . But for the hinder half there can be no doubt that the quantity of light diffused by it must be less than for the front half.

Messerschmitt finds fault with v. Lommel's theory because the influence of polarization is left out of account. To support this assertion he mentions besides his own observations those of Viole \* respecting polarization through emission. As the circumstances are so widely different (molten silver being operated upon) this cannot be used as an argument. At the outset I showed that the polarizing of the light is not a quality of diffuse reflecting substances ; when it occurs it is invariably the consequence of normal reflexion, which is a phenomenon quite apart from diffusion. Hence von Lommel was quite right in leaving polarization out of the question.

#### RESUMÉ OF RESULTS.

The investigations upon compressed powders of such thickness that no perceptible light penetrated right through them lead to the following results :—

1. Common light is not polarized by diffuse reflexion, (Lommel's hypothesis.)

2. The intensity of the light diffusely reflected under the angles  $+e$  and  $-e$  is the same, or it is independent of the azimuth. There is no normal reflexion. (Lommel's hypothesis.)

3. The law of emission by constant incidence is independent of colour, or the coefficient of diffusion is independent of the wave-length in the case of particles of the given size. (Lommel's hypothesis).

4. A law for the intensity of reflected scattered light cannot be symmetric in reference to  $i$  and  $e$ .

\* J. Viole, *Compt. Rend. ev. II.* p. 111 (1887).

5. The intensity of the diffuse reflected light with the angle  $\epsilon$  constant and with varying angles of incidence  $i$  is not proportional to the  $\cos i$ , as Lambert assumes.

6. The intensity of the diffuse reflected light with the angle  $i$  constant and the angle  $\epsilon$  varying is proportional to  $\cos \epsilon$ , or *Lambert's law of emanation is strictly correct for absolutely matt surfaces without any exception.*

7. The so-called law of the cosine ( $q = \Gamma_2 \cdot ds \cdot \cos i \cos \epsilon$ ) is not true in consequence of the deviations of the law of the  $\cos i$ . The deviations range between 4·6 per cent. and 10 per cent.

In conclusion I wish to return my best thanks to Prof. Dr. von Lommel, who drew my attention to this interesting branch of optics. I am also greatly indebted to Prof. Dr. Seeliger and Prof. Dr. Graetz for the interest shown by these gentlemen.

Munich, Physical Laboratory of the University,  
December 1899.

*XIV. On the Theory of the Function of the Condenser in an Induction-Coil. By K. R. JOHNSON, Filosofie Licentiat \*.*

**I**N a memoir "On the Function of the Condenser in an Induction-Coil," T. Mizuno has published in May 1898† a research on the relation between the capacity of the condenser, the intensity of the primary current, and the secondary spark-length. His results can be theoretically explained as follows:—

If the condenser is inserted across the interruptor in the primary circuit, the extra current darts into the condenser; and if the maximum of the potential-difference in the condenser is very great, a spark takes place in the interruptor, and thus the oscillations in the circuit are diminished by the spark. If the capacity of the condenser is very large, the maximum of potential-difference in the condenser and the interruptor is small and unable to make a spark. Thus, the efficiency of the induction-coil is greatly increased by a little increasing capacity as far as the discharge by spark at the interruptor diminishes; when this spark is entirely suppressed, the efficiency of the induction-coil is greatest and the secondary spark-length a maximum. The capacity of the primary condenser being further increased, the efficiency of the induction-coil is diminished by the reason that the maximum potential-difference in the condenser is diminished

\* Communicated by the Author.

† Phil. Mag. xlv. p. 447.

and, of course, the intensity of the current. Thus we have at the moment of breaking the primary circuit the time  $t=0$ , and the intensity of the current is  $i_0 = \frac{E_0}{R}$  at the same time,  $E_0$  being the electromotive force of the battery, and  $R$  the resistance of the circuit. The potential-difference being 0 in the condenser at the time  $t=0$ , we have for the oscillatory charging and discharging the following equations:

$$\left. \begin{aligned} V &= -\frac{E_0}{RC\beta} \cdot C^{-\alpha t} \sin \beta t, \\ i &= \frac{E_0}{R \sqrt{1 - \frac{CR^2}{4L}}} \cdot C^{-\alpha t} \cos (\beta t + \sin^{-1} \alpha \sqrt{LC}). \end{aligned} \right\} \quad (1)$$

Here  $V$  is the potential-difference of the condenser and  $i$  the intensity of the primary current;  $L$  is the coefficient of self-induction of the primary circuit and  $C$  the capacity of the condenser.  $-\alpha \pm \beta \sqrt{-1}$  are the roots of the equation

$$LCz^2 + RCz + 1 = 0.$$

The capacity of the condenser is supposed to be at least as great as is required for suppressing the spark. If this condition were not satisfied, the above equations would have no signification.

Admitting that the maximum of the spark-length  $\lambda$  in the secondary circuit is proportional to the maximum of potential-difference in the primary condenser, we have from equation (1) approximately

$$\lambda = \frac{k \cdot E_0}{R \sqrt{C}} = \frac{ki_0}{\sqrt{C}}, \quad \dots \quad (2)$$

$k$  being a constant so far as the coefficient of self-induction in the primary circuit is not altered.

By means of the equation (2), the maximum of spark-length in the secondary circuit can be calculated for every capacity of the condenser that is sufficient for suppression of the spark at the interruptor of the primary.

The lengths of the secondary sparks, observed by Mizuno, and the values calculated from formula (2), are shown in Tables I. and II. (pp 218, 219).

The calculated values correspond to the observed as well as can be expected considering the uncertainty of the proportionality between spark-length and potential-difference. From this agreement it can be concluded that each of the curves, drawn up by Mizuno, is properly composed of two parts.

TABLE I.—The First Coil.

Capacity in Microfarads.	$i_0 = 2.78.$		$i_0 = 4.20.$		$i_0 = 6.84.$		$i_0 = 9.60.$		$i_0 = 14.70.$	
	$\lambda,$ Observ.	$\lambda,$ Calcul.								
0.00	.....	0.20	.....	0.25	.....	0.30	.....	0.45	.....	0.65
0.05	.....	1.62	.....	1.70	.....	1.70	.....	1.90	.....	2.30
0.10	.....	1.55	1.61	1.90	.....	2.10	.....	2.25	.....	2.90
0.20	.....	1.20	1.14	1.70	1.76	2.35	.....	2.80	.....	3.10
0.25	.....	1.10	1.02	1.55	1.57	2.35	.....	2.95	.....	3.30
0.30	.....	1.00	0.93	1.40	1.44	2.30	2.30	2.70	3.11	3.40
0.40	.....	0.90	0.81	1.20	1.24	1.95	1.99	2.55	2.69	3.10
0.45	.....	.....	.....	1.15	1.17	1.70	1.87	2.40	2.54	2.90
0.50	.....	0.80	0.72	1.10	1.11	1.70	1.78	2.40	2.41	2.70
0.60	.....	0.60	0.61	1.00	1.01	1.65	1.62	2.22	2.20	2.60
0.70	.....	0.60	0.61	0.97	0.94	1.50	1.50	2.20	2.04	2.50
0.80	.....	0.40	0.54	0.88	0.88	1.50	1.41	2.00	1.91	2.40
0.90	.....	0.38	0.51	0.88	0.83	1.35	1.33	1.90	1.80	2.35
1.00	.....	0.38	0.51	0.88	0.79	1.28	1.26	1.75	1.70	2.30

TABLE II.—The Second Coil.

Capacity in Microfarads.	$i_0 = 1\cdot80.$		$i_0 = 2\cdot55.$		$i_0 = 6\cdot00.$		$i_0 = 7\cdot05.$		$i_0 = 9\cdot00.$		$i_0 = 12\cdot90.$	
	$\lambda,$ Observ.	$\lambda,$ Calcul.										
0·00	0·40	.....	0·60	.....	0·75	.....	1·00	.....	1·10	.....	1·20	.....
0·05	1·30	.....	1·70	.....	2·40	.....	2·60	.....	2·60	.....	2·85	.....
0·10	1·50	.....	2·00	.....	3·25	.....	3·50	.....	3·60	.....	4·30	.....
0·20	1·40	1·55	2·10	.....	3·50	.....	4·50	.....	5·20	.....	6·40	.....
0·25	1·30	1·27	2·00	2·35	3·60	.....	4·90	.....	5·30	.....	7·50	.....
0·30	1·30	1·30	2·00	2·14	3·40	4·35	5·25	.....	6·30	.....	8·10	.....
0·40	1·10	1·10	1·70	1·86	3·35	3·77	5·25	.....	7·50	.....	9·60	.....
0·45	1·00	1·00	1·60	1·66	3·20	3·55	5·20	5·29	7·50	.....	10·00	.....
0·50	0·90	0·83	1·50	1·40	3·00	2·85	4·20	5·02	6·70	6·85	9·50	10·26
0·60	0·70	0·70	1·40	1·24	2·90	2·66	4·00	3·97	5·50	5·43	8·10	8·11
0·70	0·70	0·70	1·30	1·17	2·75	2·55	4·00	3·74	5·00	5·10	8·00	7·65
0·80	0·70	0·70	0·70	0·70	2·38	2·35	3·55	4·90	4·94	7·70	7·26	7·26

The first, or rising, part corresponds to a spark in opening the circuit; the second, or descending, part of the curve corresponds to the law  $\lambda = \frac{ki_0}{\sqrt{C}}$  without spark, the two

parts meeting in a point that corresponds to a maximum for the spark-length in the secondary circuit, and an *optimum* for the capacity in regard of the efficiency of the secondary coil. The two parts of the curve would probably form a cusp in the common point if a pair of pieces of graphite were inserted in the primary circuit on each side of the interruptor, the capacity being diminished gradually from its greatest value during the observations.

Stockholm, Sweden.

*XV. On the Passage of Argon through thin Films of India-rubber.* By Lord RAYLEIGH, F.R.S.\*

SOON after the discovery of Argon it was thought desirable to compare the percolation of the gas through india-rubber with that of nitrogen, and Sir W. Roberts-Austen kindly gave me some advice upon the subject. The proposal was simply to allow atmospheric air to percolate through the rubber film into a vacuum, after the manner of Graham, and then to determine the proportion of argon. It will be remembered that Graham found that the percentage of oxygen was raised in this manner from the 21 of the atmosphere to about 40. At the time the experiment fell through, but during the last year I have carried it out with the assistance of Mr. Gordon.

The rubber balloon was first charged with dry boxwood sawdust. This rather troublesome operation was facilitated by so mounting the balloon that with the aid of an air-pump the external pressure could be reduced. When sufficiently distended the balloon was connected with a large Toepler pump, into the vacuous head of which the diffused gases could collect. At intervals they were drawn off in the usual way.

The diffusion was not conducted under ideal conditions. In order to make the most of the time, the apparatus was left at work during the night, so that by the morning the internal pressure had risen to perhaps three inches of mercury. The proportion of oxygen in the gas collected was determined from time to time. It varied from 34 per cent. when the vacuum was bad to about 39 per cent. when the vacuum was good.

\* Communicated by the Author.

On an average it was estimated that the proportion of oxygen would be about 37 per cent. of the whole. The total quantity of diffused gas reckoned at atmospheric pressure was about 300 c.c. per twenty-four hours.

On removal from the pump the gas was introduced into an inverted flask standing over alkali, and with addition of oxygen as required was treated with the electrical discharge from a transformer in connexion with the public supply of alternating current. In this way the nitrogen was gradually oxidized and absorbed. Towards the close of operations the gas was transferred to a smaller vessel, where it was further sparked until no further contraction occurred, and the lines of nitrogen had disappeared from the spectrum. The excess of oxygen was then removed by phosphorus.

It remains only to record the final figures. The residue, free of oxygen and nitrogen, from 3205 c.c. of diffused gas was 39 c.c. The most instructive way of stating the result is perhaps to reckon the argon as a percentage, not of the whole, but of the nitrogen and argon only. Of the 3205 c.c. total, 2020 c.c. would be nitrogen and argon, and of this the 39 c.c. argon would be 1·93 per cent. Since, according to Kellas (Proc. Roy. Soc. vol. lix. p. 67, 1895), 100 c.c. of mixed atmospheric nitrogen and argon contains 1·19 per cent. of argon, we see that in the diffused gas the proportion of argon is about half as great again as in the atmosphere. Argon then passes the indiarubber film more readily than nitrogen, but not in such a degree as to render the diffusion process a useful one for the concentration of argon from the atmosphere.

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*XVI. On the Conductivities of certain Heterogeneous Media for a Steady Flux having a Potential.* By CHARLES H. LEES, D.Sc.\*

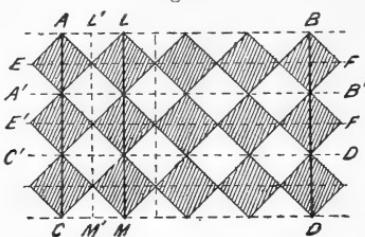
**I**N the chapter on "Conduction through heterogeneous media," in his 'Electricity and Magnetism,' Maxwell works out the conductivity of a compound medium formed by embedding in a medium of conductivity  $k_2$  a number of small spheres of a medium of conductivity  $k_1$ , for the case in which the total volume of the spheres bears only a small proportion to that of the medium  $k_2$ , and the distances of the spheres apart are so great that they have no mutual effect on one another. He also works out the conductivities for two other cases of compound media: in the first the two media are separated by planes either parallel or perpendicular to

\* Communicated by the Physical Society: read November 24, 1899.

the plane equipotential surfaces in the media ; in the second the parts of the two media consist of right prisms of rectangular cross-section, one dimension of the cross-section being infinitely great compared to the other, and the length of the prism being again infinitely great compared to this greatest cross-sectional dimension, placed with their edges either parallel or perpendicular to the equipotential surfaces. The difference of order of magnitude of the three dimensions of the elementary parts of the two media in this last case is necessary in order that the disturbance of the flow near the edges of the prism may be neglected in the calculation.

These three cases, although of considerable interest, have only a limited application on account of the restrictions introduced to enable the calculations to be carried out ; and I propose here to consider the case of a medium formed of an equal number of infinitely long prisms of square cross-section, of two media having conductivities  $k_1$  and  $k_2$ , arranged as shown in fig. 1, and bounded by two parallel equipotential

Fig. 1.

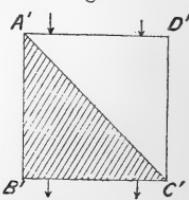


planes, AB, CD, drawn through the diagonals of the cross-sections of the prisms.

I assume that the flux and potential are continuous at the surfaces of separation of the two media. If, as in the case of the electrical potentials of copper and zinc, a difference of potential may exist between the media on the two sides of the surface of separation without a flux resulting, the potential which is continuous through the surface must be understood to be that to which the flux is due.

From symmetry it is evident in the first place that A'B', C'D', and in the second place that EF, E'F', &c., are equipotential planes. Also that AC, BD, LM, L'M', &c., are lines of flow. Hence the problem is reduced to finding the conductivity of a prism of square cross-section A'B'C'D' (fig. 2), of which A'D' and B'C' are equipotential surfaces, A'B' and D'C' lines of flow, and A'B'C' consists of a medium of conductivity  $k_2$ , A'D'C' of a medium of conductivity  $k_1$ .

Fig. 2.



If  $v_1$  and  $v_2$  are the potentials in the two media respectively, each satisfies the general condition

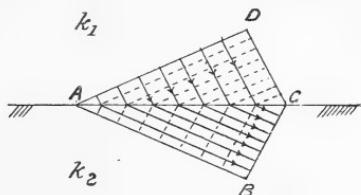
$$\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} = 0;$$

$v_1$  becomes equal to a constant along  $A'D'$ , and has no flux across  $D'C'$ ;  $v_2$  becomes constant along  $B'C'$ , and has no flux across  $A'B'$ ;  $v_1$  and  $v_2$  become identical and the fluxes due to them equal along  $A'C'$ .

It might be possible to construct two functions which would satisfy these conditions by adding together particular solutions of the above equation of the form  $v = e^{a(x \pm iy)}$ , in the way done by Riemann\*, but it is easy by a change of coordinates to make the problem depend on the following simple case, the solution of which is known.

Let  $AC$  (fig. 3) be the line of separation of two media of

Fig. 3.



conductivities  $k_1$  and  $k_2$ , and let  $AD$  be an equipotential and  $DC$  a stream-line in the  $k_1$  medium. Let  $k_1/k_2$  have such a value that  $AB$ , the stream-line in the second medium passing through  $A$ , makes the same angle with  $AC$  that  $AD$  does. If, then,  $CB$  is the equipotential line in the second medium passing through  $C$ , the triangle  $ABC$  is equal to the triangle  $ADC$ .

If  $z$  is the vector coordinate of a point in the plane of fig. 3, and  $z'$  the vector coordinate of a point in the plane of fig. 2, it is possible by a transformation  $z' = f(z)$  to convert the right-angled triangle  $ADC$  in the  $z$ -plane into the isosceles right-angled triangle  $A'D'C'$  in the  $z'$ -plane †. Similarly, the same transformation converts the triangle  $ABC$  in the  $z$ -plane into the triangle  $A'B'C'$  in the  $z'$ -plane; and contiguous points on opposite sides of  $AC$  in the  $z$ -plane become contiguous points on opposite sides of  $A'C'$  in the  $z'$ -plane. Hence the quadrilateral  $ABCD$  converts into the quadrilateral  $A'B'C'D'$ , and the difference of potential and the amount of

\* Partielle Differentialgleichungen, Abschnitt iv., Bewegung der Wärme

† Forsyth, 'Theory of Functions,' p. 543; Love, Amer. Journ. of Math. xi. pp. 164 & 168 (1889).

the flux between any two points of the area ABCD will be identical with the quantities for the corresponding points of the area A'B'C'D'.

If V is the difference of potential between the points A, C of fig. 3 and AC =  $a$ , the flux bounded by the stream-lines DC and AB

$$= k_1 \frac{a \cos \theta V}{a \sin \theta} = k_1 V \cot \theta, \text{ where } \theta = \angle DAC.$$

Hence the flux bounded by the stream-lines D'C' and A'B' in fig. 2 under the potential-difference V is equal to  $k_1 V \cot \theta$ .

If  $k$  is the apparent conductivity of the square, the flux bounded by the stream-lines D'C' and A'B' is equal to  $kV$ ; hence

$$k_1 V \cot \theta = kV, \text{ or } k = k_1 \cot \theta.$$

Now in fig. 3, since the flux is continuous across AC,  $k_1 \cot \theta = k_2 \cot BCA$ . Also  $\angle BAC = \angle DAC$ .

$$\therefore k_1 \cot \theta = k_2 \tan \theta;$$

$$\text{i.e. } \cot \theta = \sqrt{\frac{k_2}{k_1}}.$$

Therefore the apparent conductivity  $k$  of the square

$$= \sqrt{k_1 k_2}.$$

If now this medium, consisting half of material  $k_1$ , half of material  $k_2$ , be supposed homogeneous, and be combined, in the way indicated in fig. 1, with an equal volume of the  $k_1$  medium, we have  $k'$  the conductivity of the new medium,

$$= k^{\frac{1}{2}} k_1^{\frac{1}{2}},$$

$$= k_1^{\frac{1}{2}} k_2^{\frac{1}{2}}.$$

Similarly, by making other combinations of the new media and the old, we deduce that if a volume  $p_1$  of a medium of conductivity  $k_1$  be combined in this manner with a volume  $1-p_1$  of a second medium of conductivity  $k_2$ , the conductivity  $k$  of the combination will satisfy the equation

$$k = k_1^{p_1} k_2^{(1-p_1)}; \quad \dots \quad (1)$$

or

$$\log k = p_1 \log k_1 + (1-p_1) \log k_2,$$

$$= \log k_2 + p_1 \log \frac{k_1}{k_2}. \quad \dots \quad (2)$$

That is, for the mixture considered, the logarithms of the conductivities for fluxes parallel to the diagonals in fig. 1 follow the law of means.

Since  $\log k = -\log \rho$ , where  $\rho$  is the resistivity of a medium, we also have

$$\begin{aligned}\log \rho &= p_1 \log \rho_1 + (1-p_1) \log \rho_2 \\ &= \log \rho_2 + p_1 \log \frac{\rho_1}{\rho_2} . . . . . \quad (3)\end{aligned}$$

as the relation between the resistivity of the mixture and the resistivities and relative volumes of its constituents.

If more than two media are present in volumes  $p_1, p_2, p_3, \dots$  per c.c. of the mixture,

$$k = k_1^{p_1} \cdot k_2^{p_2} \cdot k_3^{p_3} \dots . . . . . \quad (4)$$

In order to show the principal features of the distribution of the flux and potential in a medium consisting of equal square prisms of two media arranged as indicated in fig. 1, the equipotential lines (or the stream-lines) for the single

Fig. 4.

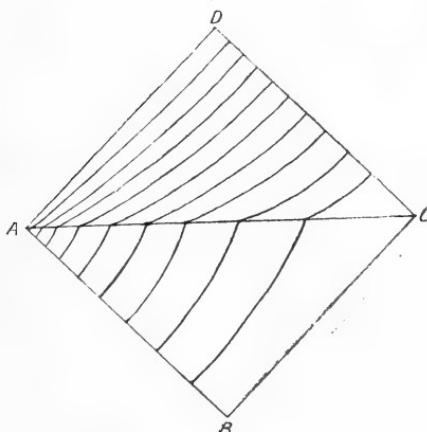
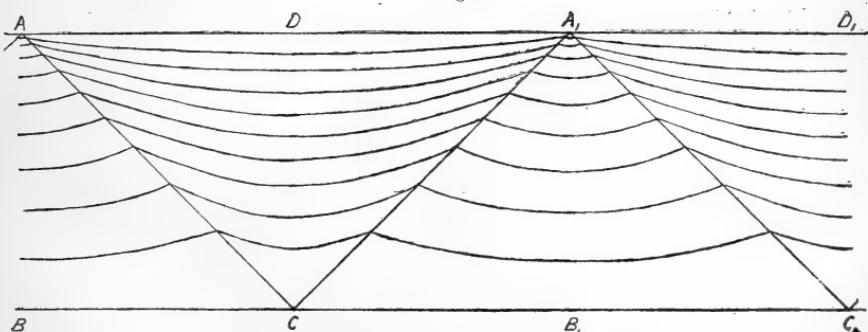


Fig. 5.



block considered above are shown in fig. 4, and for a strip of the medium in fig. 5. In each case one constituent conducts

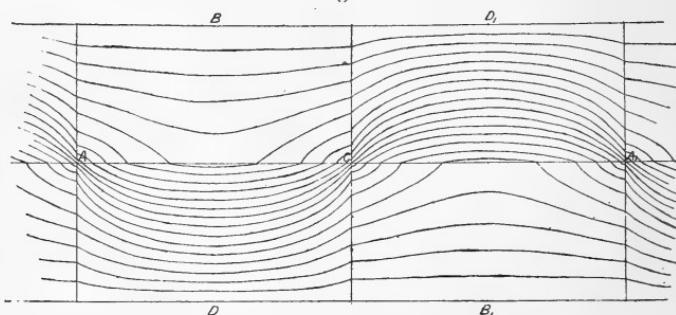
six times as well as the other. The curves have been drawn by an approximate method which depends on the fact that near each angular point A, C, the equation which transforms the kite-shaped figure of fig. 3 into the square of fig. 2 takes the form  $z' = Az^n$ . The accuracy of the diagrams will therefore be least near the centre of each square ABCD, where the position of an equipotential line may be in error by 10 per cent. of its distance from the next one.

Professor Lamb has pointed out to me that by superposing a second flux, the direction of which is at right angles to the first, on the first, a flux with stream and equipotential lines through the centres of the squares parallel to their sides is obtained. The conductivity of the medium for this flux will be readily seen to be given again by the formula

$$k = \sqrt{k_1 k_2}.$$

The equipotential lines (or the stream-lines) for a strip of the medium, when one constituent conducts six times as well as the other, are shown in fig. 6.

Fig. 6.



Since there are four directions in the medium in which the conductivity has the above value, the conductivity of the medium for a flux in any direction has the same value, *i.e.* equation (4) gives the conductivity of a compound medium in the general case where the constituents are present in the form of long prisms with their axes perpendicular to the planes of flow.

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### XVII. *The Law of Partition of Kinetic Energy.*

By S. H. BURBURY\*.

ORD RAYLEIGH'S article† seems to raise the question what is the enunciation of the Maxwell-Boltzmann law of equal partition of energy. It cannot mean that in every case in which a number of particles of unequal masses are in stationary motion each particle has the same mean

\* Communicated by the Author.

† *Suprà*, p. 98.

kinetic energy. For it is easy to construct a system in which that is not true. For instance, suppose two parallel fixed elastic planes, P and Q, and PQ a common normal. Let  $m$  and M be two elastic spheres of unequal masses, each having its centre in the line PQ. Initially let  $m$  be touching the plane P and be projected in direction PQ. Simultaneously let M be touching the plane Q and be projected in direction QP. The two spheres will collide, having their line of centres in PQ, with the point of contact, say, at R. If the momenta are equal and opposite, the two spheres will, after collision, retrace their respective courses, will rebound normally from the two planes, and will again collide at the same place, and so on for ever. Since the momenta are equal and the masses unequal, the kinetic energies are unequal. Yet the motion is stationary. The condition of stationary motion is then not a sufficient foundation for the theorem of equal partition of energy. What further condition is necessary or sufficient?

It is generally understood that the theorem is proved in the Kinetic Theory of Gases, the simplest form of which may be stated thus :—

A very great number of elastic spheres are moving in a bounded space, and freely by their encounters or collisions exchanging energy with one another. Let no forces act except during collisions between two spheres, or between a sphere and the bounding surface, supposed perfectly elastic. Let  $f(u, v, w) du dv dw$  or  $f \cdot du dv dw$  be at any instant the number of spheres  $m$  whose component velocities lie within the limits

$$u \dots u + du \text{ &c.} \dots \dots \dots \quad (1)$$

Similarly, let  $F(U, V, W) dU dV dW$  or  $F \cdot dU dV dW$  be the number of spheres M whose component velocities lie at the same instant within the limits

$$U \dots U + dU \text{ &c.} \dots \dots \dots \quad (2)$$

If  $m$  and M, having these velocities, are properly situated with respect to one another, they will within the time  $dt$  after the given instant collide with each other, and assume new velocities denoted by the accented letters  $u'$  &c.  $U'$  &c. where

$$\begin{aligned} m(u^2 + v^2 + w^2) + M(U^2 + V^2 + W^2) = & m(u'^2 + v'^2 + w'^2) \\ & + M(U'^2 + V'^2 + W'^2). \end{aligned}$$

Boltzmann now says that it is necessary to make a special assumption. And the assumption he does make is that the motion is, and continues to be, *molecular ungeordnet* (see *Vorlesungen über Gastheorie*, Part I.). The state "molecular ungeordnet" is not completely defined, perhaps because if it

were so defined, it would *eo ipso facto* cease to be "molecular ungeordnet." But the working assumption which he actually makes use of in the special case, as a deduction from his general assumption, is the same as that used by Dr. Watson and other writers, namely that, regarding  $f$  and  $F$  as the chances that a molecule shall have velocities between the limits (1) or (2), these chances are independent of the relative position of the molecules—at least that this is the case for molecules approaching collision. Hence  $f$  and  $F$  being independent, the number per unit of volume and time of collisions between members of the class  $f$  and members of the class  $F$  is proportional to  $Ff$ . And from this, by a well-known method, it is proved that

$$\frac{f}{F} = \frac{c e^{-\hbar m(u^2+v^2+w^2)}}{C e^{-\hbar M(U^2+V^2+W^2)}},$$

and therefore  $\overline{mu^2} = \overline{MU^2}$  &c., which is the law.

But the question arises whether the state of things assumed by Boltzmann to exist, from which the theorem of equal partition of energy follows as a mathematical deduction, can exist, and continue to exist, in fact in a finite system of molecules left to their own mutual actions for infinite time undisturbed from without.

I think Lord Rayleigh's argument, p. 109 *et seq.*, requires some assumptions :—

- (1) Systems on the same path move independently of one another.
- (2) Systems cannot exchange paths ; or if they can we must assume a law of interchange.

I think there may be other constants besides  $E$ , *e. g.* if two elastic spheres with velocities  $u_1, u_2$ , &c. collide,  $u_1u_2 + v_1v_2 + w_1w_2$  is constant as well as  $E$ .

Does not the method prove too much ? namely that not merely the law of equal partition (p. 115), but in effect the distribution  $e^{-\hbar E}$  must hold for all states of matter.

XVIII. *Notes on the Electromagnetic Theory of Light.—I. Geometrical Properties of the Wave-Surface &c. II. Reflexion and Refraction at the Boundary of Crystals, treated by a Theorem of Sir William Rowan Hamilton.* By Prof. A. McAULAY, University of Tasmania\*.

#### 1. Geometrical Properties of the Wave-Surface &c.

**M**R. OLIVER HEAVISIDE ('Electrical Papers,' vol. ii. p. 1; Phil. Mag. xix. June 1885, p. 397) first, I believe, investigated the properties of the general electro-

\* Communicated by the Author. To be read at the Meeting of the Australasian Association for the Advancement of Science, January 1900.

magnetic wave-surface. The present writer (*Phil. Mag.* xlii. Sept. 1896, p. 224) pointed out that it is an orthogonal projection—in two different ways—of the Fresnel surface. I do not know of other writers who have contributed to this particular department; but I suspect that this is due to my ignorance, and not to the absence of literature.

The following statements are either explicitly made in, or are obviously deducible from, the text of Basset's 'Physical Optics.' In that particular form of Maxwell's Electro-Magnetic Theory of Light in which the media are supposed to be non-magnetic, we have exactly the same analytical conditions, so far as plane waves in a non-absorbent medium are concerned, as in three other theories of light, viz.: (1) Fresnel's (2) MacCullagh's, (3) Lord Kelvin's (contractile aether). To be more precise:—(1) The electromagnetic displacement,  $\mathbf{D}$ , is the exact mathematical equivalent of Fresnel's displacement; (2) the electromagnetic M.M.F.,  $\mathbf{H}$  (or, what is the same in the present case, the magnetic induction  $\mathbf{B}$ ), is the exact mathematical equivalent of MacCullagh's displacement; (3) the electromagnetic E.M.F.,  $\mathbf{E}$ , is the exact mathematical equivalent of Lord Kelvin's displacement.

*In the second and third cases the mathematical equivalence extends, not only to the properties of plane waves within a medium, but also to the boundary conditions between two media. This is true in the first case also, in so far that the laws of reflexion and refraction at the boundary of isotropic transparent media, which result from the two theories, are the same.*

If only for this extraordinary property of being mathematically equivalent to so many distinct and celebrated theories, the electromagnetic theory is worthy of study.

It is to be remarked that it is only a particular form (certainly a very general particular form) of the electro-magnetic theory which has these wide and exact mathematical analogies with other theories. Mr. Heaviside has taught us to look, in Electromagnetism, for a symmetrical dual interpretation of results, the electric and magnetic quantities providing the duality. It may be anticipated that in the general electromagnetic theory of light, insight will be obtained by adhering to the symmetrical dual interpretation.

This first part of the present paper is mainly concerned with geometrical properties of the wave-surface exhibiting this symmetry. Incidentally a new presentation of the fundamental analysis will be given.

Four geometrical theorems are enunciated, and immediately after the enunciation of each, some of its obvious geometrical consequences are detailed. The proofs of the propositions are then given.

*Terminology and Notation.*—Intensity is understood to mean energy per unit volume. **D**, **E**, **B**, **H** each  $-(\text{intensity})^{\frac{1}{2}}$  will be denoted by  $\delta$ ,  $\epsilon$ ,  $\beta$ ,  $\gamma$  respectively. If it is thought desirable to give names to these vectors, they may be called the quasi-unit displacement, the quasi-unit E.M.F., &c. The terms **D**-oid, **E**-oid, &c. used in Prop. I. below may be regarded as convenient abbreviations of displacement-ellipsoid, E.M.F.-ellipsoid, &c. The vector of ray-velocity and the index-vector will be denoted by  $\rho$ ,  $\sigma$  respectively; that is to say, the magnitude of  $\rho$  is the velocity of propagation of a *ray* parallel to  $\rho$ , and the magnitude of  $\sigma$  is the reciprocal of the corresponding *wave-front* velocity,  $\sigma$  itself being perpendicular to the wave-front and in the direction of its motion. The locus of the extremities of  $\rho$  and  $\sigma$ , supposed drawn from a given origin  $O$ , are, as usual, called the wave- and index-surfaces respectively. To fix the ideas, we may suppose the unit of length to be 1 cm., and the unit of time to be  $1 (3 \times 10^{10})$  of a second. Thus *in vacuo* both wave- and index-surfaces will be spheres each of about 1 cm. radius.

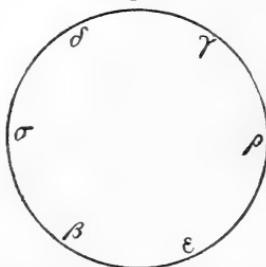
Prop. I. *The loci of the extremities of  $\delta$ ,  $\epsilon$ ,  $\beta$ ,  $\gamma$ , supposed all drawn from  $O$ , are ellipsoids with common centre  $O$ .* These ellipsoids will be called the **D**-oid, **E**-oid, **B**-oid, and **H**-oid respectively.

Prop. II. *The **D**-oid and **E**-oid are reciprocal polars; and  $\delta$  and  $\epsilon$  are corresponding vectors of them.* [S $\delta\epsilon = -1$ , 0 = S $\delta d\epsilon = S\epsilon d\delta$ .]

*The **B**-oid and **H**-oid are reciprocal polars; and  $\beta$  and  $\gamma$  are corresponding vectors of them.* [S $\beta\gamma = -1$ , 0 = S $\beta d\gamma = S\gamma d\beta$ .]

*The wave-surface and index-surface are reciprocal polars; and  $\rho$  and  $\sigma$  are corresponding vectors of them.* [S $\rho\sigma = -1$ , 0 = S $\rho d\sigma = S\sigma d\rho$ .] [See fig. 4 below.]

Fig. 1.



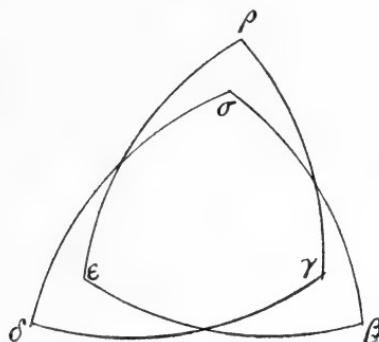
The last of these three statements results of course from the definitions of the vector of ray-velocity and of the index-vector. It is given here merely to bring out the similarities between the six vectors.

If the symbols  $\rho, \gamma, \delta, \sigma, \beta, \epsilon$  be arranged in this cyclic order (counter-clockwise in fig. 1) uniformly round a circle, it will be noticed that the three pairs of corresponding vectors mentioned in Prop. II. are those at extremities of diameters. And further :—

*Prop. III. When so arranged, each vector is the vector-product of its two neighbours taken in the cyclic order named.* That is to say,  $\rho = V\epsilon\gamma$ ,  $\gamma = V\rho\delta$ , &c.

For some purposes—especially to see easily the simplifications which occur when  $\mathbf{B}$  is parallel to  $\mathbf{H}$ —it is better to

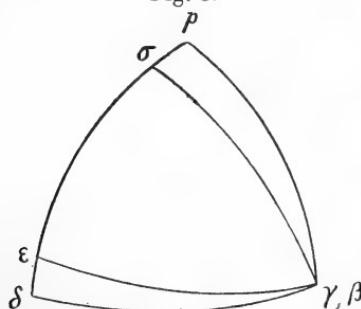
Fig. 2.



illustrate this by fig. 2. The curved lines of this figure are meant to represent quadrantal arcs on a sphere (looked at from the outside), and the points marked  $\rho, \gamma, \dots$  are the points where lines from the centre parallel respectively to the vectors  $\rho, \gamma, \dots$  meet the sphere.

When  $\mathbf{B}$  is parallel to  $\mathbf{H}$  it will be noticed that fig. 2 becomes fig. 3.

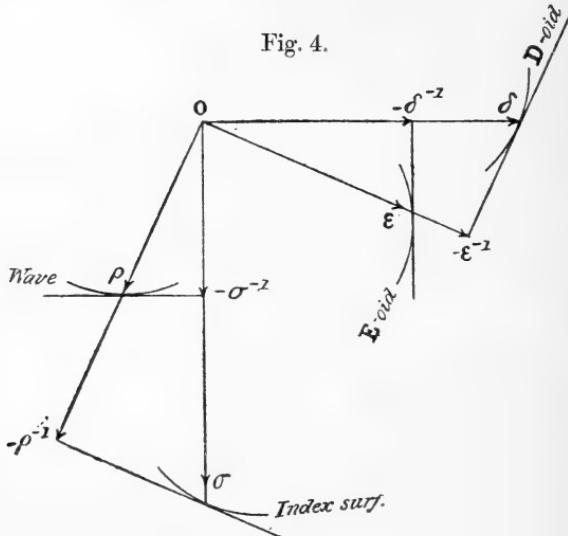
Fig. 3.



In fig. 4 the plane of the paper is taken as the plane which, in fig. 3, contains  $\rho, \sigma, \epsilon, \delta$ . In this case  $\beta$  and  $\gamma$  must be drawn upwards from O. The figure indicates the mutual

relations of  $\rho$ ,  $\sigma$ ,  $\delta$ , and  $\epsilon$  and the corresponding surfaces, as given by Prop. II. An inspection of the figure shows that  $\delta$  is parallel to the projection of the ray on the wave-front,

Fig. 4.



that  $\epsilon$  is parallel to the projection of  $\sigma$  on the tangent-plane of the index-surface, and that  $\mathbf{H}$  and  $\mathbf{B}$  are perpendicular to all the other vectors.

By Prop. II. it will be noticed that not more than three of the six surfaces, wave-,  $\mathbf{D}$ -oid, &c., are independent. As a matter of fact two, and but two, are. These may be taken as the  $\mathbf{E}$ -oid and  $\mathbf{H}$ -oid (or as the  $\mathbf{D}$ -oid and  $\mathbf{B}$ -oid); for when these are given, the  $\mathbf{D}$ -oid and  $\mathbf{B}$ -oid are given by Prop. II., and the wave-surface and index-surface by Prop. IV.

Prop. IV.  $\epsilon$  and  $\gamma$  are, in direction, conjugate to one another, with regard to both the  $\mathbf{E}$ -oid and  $\mathbf{H}$ -oid.

$\delta$  and  $\beta$  are, in direction, conjugate to one another, with regard to both the  $\mathbf{D}$ -oid and  $\mathbf{B}$ -oid.

This proposition (when the  $\mathbf{E}$ -oid and  $\mathbf{H}$ -oid are given) suffices to determine all of the four  $\epsilon$ ,  $\gamma$ ,  $\delta$ ,  $\beta$  when the direction of any one is given. For the ellipsoids serve by Prop. I. to give the magnitude of each when its direction is known, so that it is only necessary to determine the direction of each. Suppose the direction of  $\epsilon$  given : since  $\gamma$  is conjugate to  $\epsilon$  with regard to the  $\mathbf{E}$ -oid,  $\gamma$  is confined to one plane; since it is also conjugate with regard to the  $\mathbf{H}$ -oid, it is confined to another plane. Its direction therefore is determinate. [Its sense may have either of the two values

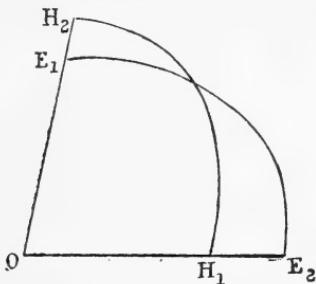
corresponding to this direction; but on account of the relation  $\rho = V\epsilon\gamma$ , the senses will correspond to propagations of disturbance in opposite directions.] When  $\epsilon$  and  $\gamma$  are known,  $\delta$  and  $\beta$  are known by Prop. II.

Also, when  $\epsilon$  and  $\gamma$  are known,  $\rho$  is known; since  $\rho = V\epsilon\gamma$ , and also  $\sigma$ , since  $\sigma = V\delta\beta$ . Thus when the direction of any one of the four  $\epsilon$ ,  $\gamma$ ,  $\delta$ ,  $\beta$  is known, all six vectors are known.

But Prop. IV. also suffices to determine all six when the direction of  $\rho$  or of  $\sigma$  is known, and gives us geometrical constructions for the wave- and index-surfaces.

Thus if the direction of  $\rho$  is given, the plane of  $\epsilon$  and  $\gamma$  (which is perpendicular to  $\rho$ ) is given. This plane cuts the **E**-oid and **H**-oid in known ellipses, with regard to both of which  $\epsilon$  and  $\gamma$  are conjugate. Let (fig. 5)  $O H_1 E_2$ ,  $O E_1 H_2$

Fig. 5.



be the common conjugate semi-diameters of these ellipses,  $O E_1$ ,  $O E_2$  belonging to the **E**-oid, and  $O H_1$ ,  $O H_2$  to the **H**-oid.  $\epsilon$  may be either  $\pm \overline{OE}_1$  or  $\pm \overline{OE}_2$ . If we take  $\epsilon = \overline{OE}_1$ , then  $\gamma = \pm \overline{OH}_1$ , since  $\gamma$  and  $\epsilon$  are conjugate. It will thus be seen that  $\rho$  has any one of the four values given by

$$\rho = \pm VOE_1 \cdot OH_1 \quad \text{or} \quad \pm VOE_2 \cdot OH_2.$$

By taking all possible directions for  $\rho$ , this gives a geometrical construction for the wave-surface. From the construction it is clear that the surface forms a double sheet with centre at  $O$ . Fresnel's construction is clearly what the present construction degenerates into when one of the ellipsoids is a sphere.

Of course similar remarks apply to the index-surface as depending on the **D**-oid and **B**-oid.

Take  $\epsilon = \overline{OE}_1$ ,  $\gamma = \overline{OH}_1$ . Then by Prop. II.  $-\delta^{-1}$ ,  $-\beta^{-1}$  are the perpendiculars from  $O$  on the tangent-planes at  $E_1$  and  $H_1$  to the **E**-oid and **H**-oid. Since  $\sigma = V\delta\beta$  the wave-front, supposed drawn through  $O$ , contains both these normals,

*i. e.* it is the plane perpendicular to the line of intersection of the tangent planes. Further, since  $\delta = V\gamma\sigma$ ,  $\beta = V\sigma\epsilon$  [Prop. III.] the directions of  $\delta$  and  $\beta$  are given by saying that they are in the wave-front perpendicular to the projections of  $\gamma$  and  $\epsilon$  respectively on the wave-front. Thus the directions of all six vectors are given by fig. 5, and the line of intersection of the tangent planes at  $E_1$  and  $H_1$ .

If the two ellipses of fig. 5 are similar and similarly situated, the directions of  $\epsilon$  and  $\gamma$  are those of any two conjugate diameters of either ellipse. Since the area of the circumscribing parallelogram of either ellipse is constant we get but one value of  $\rho (= V\epsilon\gamma)$ , including of course its opposite.

The above construction for the wave-front still holds; and we see that the front must, in this case, touch a cone. It is a simple problem, directly from the geometrical construction, to show that this cone is of the second degree. That there is but one pair of directions (and their opposites) of  $\rho$  giving this case, is most easily seen by orthogonally projecting the **H**-oid into a sphere, when we fall on the usual case, as depending on the circular sections of the ellipsoid into which the **E**-oid has been projected. The geometrical properties connected with conical refraction can thus be treated by the present method. This brief indication of the fact must suffice.

It might be thought that these generalizations of the particular form of theory usually adopted would necessitate a complex proof. On the contrary, it will be found, I think, that the following proofs are simpler than those ordinarily given for the particular form.

From Maxwell's 'Theory of Electromagnetism' we take the following; omitting the  $4\pi$ 's, as recommended by Mr. Heaviside, in such work as the present,

$$\dot{\mathbf{D}} = V \nabla \mathbf{H}, \quad \dot{\mathbf{B}} = -V \nabla \mathbf{E}, \quad \dots \quad (1)$$

$$\mathbf{D} = c\mathbf{E}, \quad \mathbf{B} = \mu\mathbf{H}, \quad \dots \quad (2)$$

where  $c$ ,  $\mu$  are self-conjugate linear vector-functions of a vector (permittivity and permeability), and

$$\frac{1}{2}(\mathbf{S}\mathbf{D}\mathbf{E} + \mathbf{S}\mathbf{B}\mathbf{H}) = -w, \quad \dots \quad (3)$$

where  $w$  is the energy per unit volume, *i. e.* the "intensity."

The only kind of wave we contemplate is a plane wave in which the quantities have constant value over the wave-front.

Take the axis of  $z$  as normal to the front and  $k$  as the unit vector in that direction. Denote partial differentiation by  $D_z$  &c. Thus if a wave with velocity  $v$  can be propagated in

that direction, we shall have

$$\mathbf{H} \text{ (or } \mathbf{E} \text{ &c.)} = \text{function } (z - vt),$$

and for any such function

$$\mathbf{D}_t = -v\mathbf{D}_z, \quad \nabla = k\mathbf{D}_z.$$

Thus (1) becomes

$$\nabla k\mathbf{D}_z\mathbf{H} = -v\mathbf{D}_z\mathbf{D}, \quad \nabla k\mathbf{D}_z\mathbf{E} = v\mathbf{D}_z\mathbf{B};$$

or putting, in accordance with the definition of  $\sigma$  as an index-vector

$$kv^{-1} = \sigma, \quad \mathbf{D} = -\nabla\sigma\mathbf{H}, \quad \mathbf{B} = \nabla\sigma\mathbf{E}. \quad \dots \quad (4)$$

By (4) and (3),

$$\mathbf{S}\mathbf{D}\mathbf{E} = \mathbf{S}\sigma\mathbf{E}\mathbf{H} = \mathbf{S}\mathbf{B}\mathbf{H} = -w. \quad \dots \quad (5)$$

By (4) and (5),

$$\nabla\mathbf{D}\mathbf{B}/w = \sigma. \quad \dots \quad (6)$$

So far we have been practically following Mr. Heaviside.

By (2),

$$\mathbf{S}\mathbf{D}d\mathbf{E} = \mathbf{S}\mathbf{E}d\mathbf{D}, \quad \mathbf{S}\mathbf{B}d\mathbf{H} = \mathbf{S}\mathbf{H}d\mathbf{B}.$$

Hence by (5)

$$-\frac{1}{2}dw = \mathbf{S}\mathbf{D}d\mathbf{E} = \mathbf{S}\mathbf{E}d\mathbf{D} = \mathbf{S}\mathbf{B}d\mathbf{H} = \mathbf{S}\mathbf{H}d\mathbf{B}. \quad \dots \quad (7)$$

Now define  $\rho$  by the equation

$$\nabla\mathbf{E}\mathbf{H}/w = \rho. \quad \dots \quad (8)$$

By (5),

$$\mathbf{S}\sigma\rho = -1. \quad \dots \quad (9)$$

By (4),

$$\begin{aligned} \mathbf{S}\mathbf{H}d\mathbf{B} &= \mathbf{S}\mathbf{H}d\nabla\sigma\mathbf{E} = \mathbf{S}\mathbf{H}\sigma d\mathbf{E} + \mathbf{S}d\sigma\nabla\mathbf{E}\mathbf{H} \\ &= \mathbf{S}\mathbf{D}d\mathbf{E} + w\mathbf{S}\rho d\sigma. \end{aligned}$$

Hence by (7) and (9),

$$\mathbf{S}\rho d\sigma = 0, \quad \mathbf{S}\sigma d\rho = 0. \quad \dots \quad (10)$$

This shows that the locus of the extremity of  $\rho$  and that of  $\sigma$  are polar reciprocals, and therefore that  $\rho$  is the vector of ray velocity.

Putting now, in accordance with our first definitions,

$$\mathbf{D} = \delta \sqrt{w}, \quad \mathbf{E} = \epsilon \sqrt{w}, \quad \mathbf{B} = \beta \sqrt{w}, \quad \mathbf{H} = \gamma \sqrt{w}, \quad \dots \quad (11)$$

and re-writing (4) to (8)

$$\delta = V\gamma\sigma, \beta = V\sigma\epsilon, \dots \dots \dots \dots \dots \quad (12)$$

$$S\delta\epsilon = S\beta\gamma = -1, \dots \dots \dots \dots \dots \dots \quad (13)$$

$$\sigma = V\delta\beta, \dots \dots \dots \dots \dots \dots \dots \quad (14)$$

$$0 = S\delta d\epsilon = S\epsilon d\delta = S\beta d\gamma = S\gamma d\beta, \dots \dots \dots \quad (15)$$

$$\rho = V\epsilon\gamma, \dots \dots \dots \dots \dots \dots \dots \quad (16)$$

From (2) and (11)

$$\delta = c\epsilon, \beta = \mu\gamma, \dots \dots \dots \dots \dots \dots \quad (17)$$

Hence from (13),

$$\left. \begin{aligned} S\epsilon c\epsilon &= -1, & S\gamma\mu\gamma &= -1, \\ S\delta c^{-1}\delta &= -1, & S\beta\mu^{-1}\beta &= -1. \end{aligned} \right\} \dots \dots \dots \dots \dots \quad (18)$$

This is Prop. I. Prop. II. is contained in equations (9), (10), (13), (15). Prop. III. is contained in equations (12), (14), (16), and

$$\epsilon = V\beta\rho, \gamma = V\rho\delta, \dots \dots \dots \quad (19)$$

which are simple deductions from (16), (12), (13).

To prove Prop. IV. notice that equations (18) are the equations of the **E**-oid, **H**-oid, **D**-oid, and **B**-oid respectively. From the equations

$$S\beta\epsilon = 0, \quad S\delta\gamma = 0$$

[Prop. III. or eq. (12)] we have by (17)

$$S\epsilon\mu\gamma = 0, \quad S\gamma c\epsilon = 0,$$

which express that  $\epsilon$  and  $\gamma$  are conjugate to one another with regard to the **H**-oid and with regard to the **E**-oid [these being  $S\gamma\mu\gamma = -1$ ,  $S\epsilon c\epsilon = -1$ , respectively]. Similarly for  $\delta$  and  $\beta$ .

All these geometrical properties have been proved without finding the equations of the wave-surface and index-surface, and the other well-known properties of the wave-surface can be similarly proved. But of course for some purposes it may be desirable to find these equations.

The finding of the equation of the index-surface (by essentially the same method as Mr. Heaviside's) may be thus put

$$\begin{aligned} c\epsilon = \delta &= V\gamma\sigma = V(\mu^{-1}\beta\sigma) = -V\sigma\mu^{-1}V\sigma\epsilon \\ &= -m^{-1}\mu V\mu\sigma V\sigma\epsilon, \end{aligned}$$

where  $m$  is the product of the three principal permeabilities. Thus

$$m\mu^{-1}c\epsilon = \sigma S\epsilon\mu\sigma - \epsilon S\sigma\mu\sigma,$$

therefore  $\epsilon/S\mu\sigma = (m\mu^{-1}c + S\sigma\mu\sigma)^{-1}\sigma,$

whence, operating by  $S\mu\sigma( \ )$ ,

$$1 = S\sigma\mu(m\mu^{-1}c + S\sigma\mu\sigma)^{-1}\sigma,$$

and this may be put in a variety of forms, as usual. But the interesting thing to notice is that by the above method it is obvious that by a similar process the equation of the wave-surface is

$$1 = S\rho\mu^{-1}(m^{-1}\mu c^{-1} + S\rho\mu^{-1}\rho)^{-1}\rho,$$

and that this has been arrived at without any complex integration of (9) and (10).

In concluding this part of the paper I may remark that the above methods can be applied to other theories of light. They are not quite so naturally applicable because in such theories—without exception as far as I know—only one of the pairs of vectors  $\delta, \epsilon$  and  $\beta, \gamma$  obviously presents itself, and the other pair must be deliberately introduced by definition. In the electromagnetic theory both pairs are present before the special problems connected with optics are considered.

## II. *Reflexion and Refraction at the Surface of Crystals, treated by a Theorem of Sir Wm. Rowan Hamilton.*

In his 'Elements of Quaternions' (423 (12) in 1st edition, probably this important theorem will not escape the editor of the 2nd edition) Hamilton has proved a theorem of such singular beauty and ease of application in particular cases, that I think it well worth calling attention to. This seems the more necessary as it appears to have been overlooked by subsequent writers.

His treatment is—probably necessarily, based as it is on MacCullagh's theory—somewhat complex, whereas the treatment on the electromagnetic theory is little more than an interpretation of the fundamental equations. He treats only of the case where a ray in an isotropic medium is incident on the face of a crystal, and where the polarization of the incident light is such that there is but one refracted ray. On the electromagnetic theory it is just as easy to suppose both media to be crystalline, and to allow the incident polarization to be arbitrary.

There will in this case be one incident ray, two refracted rays, and two reflected rays, five in all as against Hamilton's (and MacCullagh's, since in this particular Hamilton is following MacCullagh) three.

Let the M.M.F.'s of the five rays at the point of incidence

(taken as the point called O above) at any instant be, in order,

$$\mathbf{H}, \mathbf{H}_1', \mathbf{H}_2', \mathbf{H}_1'', \mathbf{H}_2'',$$

and the corresponding vectors of ray-velocity

$$\rho, \rho_1', \rho_2', \rho_1'', \rho_2'',$$

and similarly for the other vectors involved.

The theorem is true only for the usual form of electromagnetic theory, *i.e.* for the case when both media are assumed non-magnetic. It is to be remembered that this form is apparently as satisfactory as the more general form in explaining all known optical phenomena. The following is the theorem :—

*If we suppose mechanical forces*

$$\mathbf{H}, -\mathbf{H}_1', -\mathbf{H}_2', \mathbf{H}_1'', \mathbf{H}_2''$$

*to act at points whose vector coordinates are*

$$\rho, \rho_1', \rho_2', \rho_1'', \rho_2'',$$

*they will reduce to a couple whose plane is parallel to the face.*  
 [See figures 6 and 7 below.]

Before giving the proof some remarks are desirable. If the incident wave-front and the two wave-surfaces (centre at point of incidence) be given, by Huyghens's construction we know the five wave-fronts. These fronts, supposed drawn touching the wave-surfaces at the appropriate points, all contain the line of intersection of the incident front with the face, or as we shall call it the trace of that front on the face. Since the fronts are known the directions of the M.M.F.'s are known, and it only remains to find their magnitudes. These M.M.F.'s, drawn as described in the enunciation, are in the corresponding fronts, and therefore all intersect one line, the trace.

Thus when the circumstances of incidence are given the four magnitudes of the M.M.F.'s of the refracted and reflected waves are required. The theorem gives five conditions, but one of them is always satisfied by reason of the five vectors all intersecting one line. The theorem is in every case not only necessary, but sufficient to determine the unknown quantities.

In the proof about to be given, whenever  $\Sigma \pm ( )$  is applied to a sum, referring to the five rays, the sign + is to be understood to refer to one medium, and the sign — to the other.

Let  $k$  be the unit normal of the face. The boundary conditions are that the tangential components of  $\mathbf{H}$  and  $\mathbf{E}$ , and

the normal components of  $\mathbf{B}$  and  $\mathbf{D}$ , are continuous. Thus

$$0 = \Sigma \pm V k \mathbf{H}, \quad 0 = \Sigma \pm V k \mathbf{E} = \Sigma \pm V k V \rho \mathbf{B}$$

[Prop. III.],

$$0 = \Sigma \pm S k \mathbf{B}, \quad 0 = \Sigma \pm S k \mathbf{D}.$$

[Here we have apparently six conditions to determine four unknowns. That the two last conditions are contained in the others may be thus shown:— $\sigma$ ,  $\sigma'_1$ ... are perpendicular to the fronts and therefore to the trace. Their components parallel to the face are equal; for expressing that the foot of the perpendicular from O on the trace is in each front

$$-1 = S \alpha \sigma = S \alpha \sigma'_1 = \dots,$$

where  $\alpha$  is the vector perpendicular from O on the trace. Hence

$$V k \sigma = V k \sigma'_1 = \dots = \eta,$$

say, where  $\eta$  is parallel to the trace. But

$$\Sigma \pm S k \mathbf{B} = \Sigma \pm S k \sigma \mathbf{E} = \Sigma \pm S \eta \mathbf{E} = 0$$

by the condition  $\Sigma \pm V k \mathbf{E} = 0$ . Similarly the condition  $\Sigma \pm S k \mathbf{D} = 0$  can be deduced from  $\Sigma \pm V k \mathbf{H} = 0$ . We shall, however, use the condition  $\Sigma \pm S k \mathbf{B} = 0$ .]

Make now the assumption that the media are non-magnetic, *i.e.* that  $\mathbf{B}$  is parallel and proportional to  $\mathbf{H}$ . In this case both normal ( $\Sigma \pm S k \mathbf{B} = 0$ ) and tangential ( $\Sigma \pm V k \mathbf{H} = 0$ ) components of  $\mathbf{H}$  are continuous, *i.e.*

$$\Sigma \pm \mathbf{H} = 0.$$

Also from the condition  $\Sigma \pm V k \mathbf{E} = 0$ ,

$$\Sigma \pm V k V \rho \mathbf{H} = 0.$$

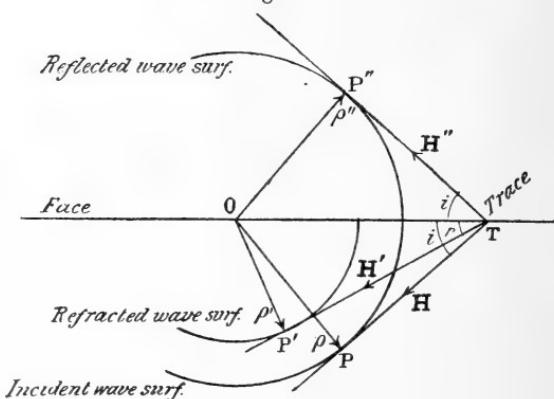
The first of these expresses that the mechanical system of the enunciation reduces to a couple. The second expresses that the vector moment of the forces about O is parallel to the normal of the face, *i.e.* that the plane of the couple is parallel to the face. This is Hamilton's theorem.

It will be noticed also that if the conditions of the enunciation are satisfied, the boundary conditions are satisfied. Thus the theorem is always sufficient to give the four unknowns.

To exhibit the ease of application in particular cases to useful interpretations take the case of two isotropic media. The theorem, it will be noticed, was not arrived at in considering this comparatively simple case, but it seems to me to serve as a much better *resumé* of our knowledge, even in this case, than any other I have come across.

First, let  $\mathbf{H}$  be in the plane of incidence, i.e. let the incident light be polarized in the plane of incidence. Fig. 6 indicates

Fig. 6.



the nature of the reflected and refracted light. The plane of incidence is the plane of the paper,  $i$  the angle of incidence, and  $r$  the angle of refraction;  $\rho, \rho', \rho''$  are the vectors of ray-velocity of the incident, refracted, and reflected light.  $\mathbf{H}$  is drawn in the incident wave-front and in the plane of incidence. It will be seen that if  $\mathbf{H}'$  and  $\mathbf{H}''$  be also drawn in the refracted and reflected fronts and in the plane of incidence, as indicated in the figure, three mechanical forces  $\mathbf{H}, -\mathbf{H}', \mathbf{H}''$  may be made to be in equilibrium, i.e. to reduce to a (null) couple whose plane is parallel to the face. By the sine rule for the equilibrium of three concurrent forces, we have

$$\frac{\mathbf{TH}}{\sin(i+r)} = \frac{\mathbf{TH}'}{\sin 2i} = \frac{\mathbf{TH}''}{\sin(i-r)},$$

in which it is to be remarked [eq. (5) above] that the intensities are proportional to the squares of the numerators and therefore to the squares of the denominators.

Fig. 6 also serves for the case when the light is polarized perpendicular to the plane of incidence.  $\mathbf{H}, \mathbf{H}',$  and  $\mathbf{H}''$  are not then as indicated in the figure, but instead they act at the points  $P, P',$  and  $P''$  of the wave-surfaces perpendicular to the plane of the paper. In order that in this case the system may reduce to a couple parallel to the face,  $\mathbf{H}$  and  $\mathbf{H}''$  must have a resultant equal and parallel to  $\mathbf{H}'$  at the same distance as  $\mathbf{H}'$  from the face and on the same side of the face. Since the distances of  $P, P',$  and  $P''$  from the face are

$$OT \cos i \sin r, OT \cos r \sin r, \text{ and } OT \cos i \sin i$$

respectively, these conditions give

$$\frac{\mathbf{TH}}{\sin 2i + \sin 2r} = \frac{\pm \mathbf{TH}''}{\sin 2i - \sin 2r} = \frac{\mathbf{TH}'}{2 \sin 2i},$$

or

$$\frac{\mathbf{TH}}{\sin(i+r) \cos(i-r)} = \frac{\mathbf{TH}'}{\sin 2i} = \frac{\pm \mathbf{TH}''}{\cos(i+r) \sin(i-r)},$$

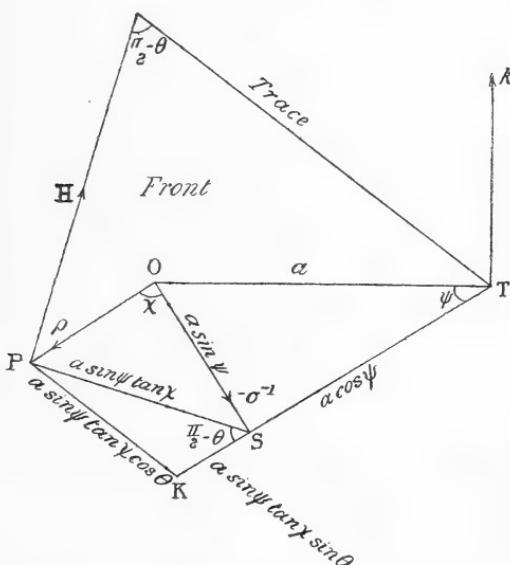
which give the ratios of the intensities in this case.

Lastly, take the case of two crystalline media. Denote in this case the angles of incidence, refraction, and reflexion by  $\psi, \psi_1', \psi_2', -\psi_1'', -\psi_2''$ .

[The angles of reflexion are called  $-\psi_1''$ ,  $-\psi_2''$  because the corresponding fronts are on the side of the face opposite to that on which are the other fronts.]

In fig. 7 let OP be the incident ray, OS the perpendicular from O on the front, OT the perpendicular on the trace, K the

Fig. 7.



point of intersection of TS and the parallel through P to the trace,  $\chi$  the angle POS between the ray and the wave normal,  $\frac{1}{2}\pi - \theta$  the angle between  $\mathbf{H}$  and the trace, and  $a$  the length of OT. Since  $\mathbf{H}$  is perpendicular to  $\rho$ , and therefore to  $\overline{PS}$ , the angle  $PSK = \frac{1}{2}\pi - \theta$ . The lengths, in terms of  $a$  and the angles, of the various lines, are sufficiently obvious from the figure.

Putting  $\mathbf{H}$  for  $\pm \mathbf{TH}$ , the components of  $\mathbf{H}$  parallel to the

*Phil. Mag. S. 5. Vol. 49. No. 297. Feb. 1900.*

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normal of the face, to OT, and to the trace are respectively

$$H \cos \theta \sin \psi, H \cos \theta \cos \psi, H \sin \theta.$$

Hence, using the theorem by resolving in these directions and taking moments round OT,

$$0 = \Sigma \pm H \cos \theta \sin \psi = \Sigma \pm H \cos \theta \cos \psi = \Sigma \pm H \sin \theta,$$

and

$$0 = \Sigma \pm H \{ \sin^2 \psi \tan \chi \cos^2 \theta + \sin \psi \sin \theta (\cos \psi + \sin \psi \tan \chi \sin \theta) \}$$

or

$$0 = \Sigma \pm H \sin \psi (\sin \psi \tan \chi + \sin \theta \cos \psi).$$

These reduce to equations (49) § 420 of Basset's 'Physical Optics' when the incident medium is isotropic.

I may remark that I believe this theorem of Hamilton's is nowhere referred to in the treatise just mentioned, nor in Lord Rayleigh's article "Wave Theory," in the *Encyclopaedia Britannica*, 9th ed., nor in Glazebrook's 'Report on Optical Theories,' in the B.A. Reports, 1885.

University of Tasmania, Hobart,  
20th November, 1899.

### XIX. *Intelligence and Miscellaneous Articles.*

CHEMICAL EFFECTS PRODUCED BY BECQUEREL'S RAYS.

BY M. P. AND MME. CURIE.

THE rays emitted by very active radiferous salts of barium are capable of converting oxygen into ozone. When the radioactive salt is kept in a stoppered bottle, a very distinct odour of ozone is perceived on opening the bottle. M. Demarçay discovered this phenomenon with some very active radiferous barium chloride which we had sent him, for his spectroscopic researches, in a little stoppered bottle. When the flask is opened the odour is incompletely dissipated; in order that it may regain its original strength it is sufficient to close the flask some ten minutes.

We have verified the production of ozone by starched potassium-iodide paper, which becomes lightly tinted when placed before the mouth of the bottle. The tint is deeper when the radiferous barium chloride is brought in contact with the paper, whilst ordinary barium chloride under the same conditions produces no effect.

The radiferous compounds necessary for the production of ozone are all very active and all luminous. The phenomenon seems more nearly related to the radioactivity than to the luminosity. Thus a very luminous carbonate of radium produces less ozone than a chloride of radium less luminous but more strongly radioactive.

We have likewise remarked a colouring action of Becquerel's rays on glass. If a radium salt is kept for some time in a glass flask, a violet coloration is perceived which appears to spread itself from the interior of the flask towards the exterior. With a

very active product, at the end of ten days the bottom of the flask, viewed from the side, is almost black where in contact with the salt. This tint diminishes in proportion as it extends into the glass, and at some millimetres depth it appears violet. With a less active product the tint is less intense and requires more time for its production. The glass of the flasks in which this phenomenon manifests itself is not blackened in the reducing flame, whence we conclude that it does not contain any lead.

The change produced in barium platinocyanide by the radium rays is probably also a chemical effect. When submitted to the action of the radium rays, barium platinocyanide begins to grow yellow, then it becomes brown, and this brown variety is less sensitive to the excitation of fluorescence. To restore the platinocyanide to its original condition it is sufficient to expose it to sunlight. This phenomenon is the same as that which has been described for the Röntgen rays by M. Villard\*.

When a layer of barium platinocyanide is placed in the dark above a layer of a radioactive salt, the platinocyanide becomes strongly luminous under the influence of the Becquerel rays; but little by little the platinocyanide is converted into the brown variety and the luminosity gradually diminishes. On exposing the system to light, the platinocyanide is partially restored, and if then the system is brought back into the dark the light emitted is again very brilliant.

Thus is realized the synthesis of a phosphorescent body with long duration of phosphorescence by means of a fluorescent body and a radioactive body.

M. Giesel has prepared a radiferous platinocyanide of barium, very luminous at the moment of its preparation, which under the action of its own Becquerel rays is converted into the less luminous brown variety †.

When the chloride of barium and radium is crystallized out of a solution which has been saturated when hot, the crystals are colourless at the moment of deposit. Little by little these crystals acquire a rose colour which becomes gradually more pronounced. This coloration appears the more rapidly and is the more intense as the salt contains more radium. If the rose crystals are dissolved the solution is colourless, and if it be caused to crystallize, it deposits crystals which are at first colourless. The development of the coloration seems to accompany that of the radioactivity, which after the deposition increases with time.

Dry chloride of barium and radium is white quite at first, it grows yellow gradually at the same time that its radioactivity develops.

It is probable that these changes of colour correspond to molecular modifications which are produced in the barium salts by the action of the radium rays.

The conversion of oxygen into ozone necessitates the expenditure

\* *Soc. de Phys.*, 18 May, 1898.

† *Wied. Ann.* lxix. p. 91.

of utilizable energy. The production of ozone by the action of the rays emitted by radium is thus a proof that this radiation represents a continual freeing of energy.—*Comptes Rendus*, t. cxxix. p. 823.

ON THE CHEMICAL ACTION OF THE X-RAYS. BY P. VILLARD.

The interesting results which M. and Mme. Curie \* have lately made known will perhaps render the following observation, which I have not ventured to publish before, of some interest.

When a Crookes tube has been in action for some time, the glass of the bulb acquires, as is well known, a very marked violet tint over the part above the plane of the anticathode, that is to say, on the side where the latter receives the cathode-rays. This region of the bulb is struck at the same time by the *x*-rays and by the diffused cathode-rays; the following experiment enables us to determine to which of the two radiations the action observed should be attributed.

In a focus-tube, I surrounded the anticathode by a wide tube, either of ordinary glass or of flint glass, the inner wall of which could be protected against the cathode-rays by very thin aluminium leaf, very transparent to the *x*-rays. A silhouette cut out of opaque metal, platinum for example, could be interposed at will in the path of these latter. After action had gone on for about half an hour I obtained the following results:

When there is no aluminium leaf the tube becomes strongly blackened if it is of flint glass, and acquires the bluish tint with metallic reflexion of flint glass that has been reduced. When it is of ordinary glass, which always contains a little lead, it only becomes brown. This is the ordinary cathodic reduction, similar to that produced in a reducing flame. The interposition of the aluminium leaf, stopping the cathode-rays, does away altogether with this reduction; and then a violet coloration is obtained, both with flint glass and with ordinary glass. This modification is evidently due to the *x*-rays; it is only produced above the plane of the anti-cathode, and if a little plate of platinum be interposed in the path of these rays, the region protected by it remains uncoloured. It was to this phenomenon that I alluded in a discussion at the Easter meeting of the Société de Physique, when I said that it was strictly speaking possible to obtain a radiograph by taking for the sensitive compound a simple glass plate.

This transformation of glass or flint glass is certainly due to oxidation, as it is equally well obtained on warming the flint glass in a strongly oxidizing flame. Very probably the violet coloration is produced by manganese; this metal, in its fully oxidized combinations, is known to colour glass violet.

These results moreover establish an analogy between the *x*-rays and the radiations emitted by radioactive substances. For this reason I propose to repeat the foregoing experiments, but substituting for ordinary glass a silicate containing, in considerable quantity, some substance whose oxidation will be easy to recognize.—*Comptes Rendus*, cxxix. p. 882.

\* *Comptes Rendus*, cxxix. p. 823; *suprà*, p. 242.

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[FIFTH SERIES.]

*MARCH 1900.*

XX. *The Striated Electrical Discharge.*  
*By J. H. JEANS\*.*

PART I.

§ 1. THE present paper is principally concerned with the appearance of light which accompanies the discharge of electricity through a rarefied gas. I have attempted to show that Prof. Thomson's "Theory of the Conduction of Electricity through Gases by Charged Ions" † is capable of supplying an explanation of the striations, and of most of the other phenomena observed in connexion with the discharge through a vacuum-tube.

Considering the case of a one-dimensional discharge between two parallel and infinite plates, Thomson has arrived at a differential equation connecting  $y$ , the semi-square of the electric intensity at a point, with  $x$ , a coordinate measured along the line of discharge. It is impossible to solve this equation in finite terms, but Thomson has drawn a graph, giving an approximate value of  $y$  for every value of  $x$ , this graph satisfying the differential equation at every point, and also the two terminal conditions at the electrodes.

In the same paper Thomson has also given a second graph, in which are plotted out the result of some measurements by Graham on the potential gradient in a vacuum-tube. The comparison of the graph thus deduced from experiment with

\* Communicated by Prof. J. J. Thomson, F.R.S.

† J. J. Thomson, Phil. Mag. xlvi. p. 253 (1899).

the graph calculated from theory is therefore of interest, and it is at once obvious that there are considerable differences between the two curves.

In particular the theoretical graph is convex to the axis of  $x$  at every point, while the experimental graph shows concavity over two regions of the axis.

Now when a graph for  $y$  is drawn from measurements actually taken from a tube through which a discharge is passing, a comparison of the graph so obtained with the glowing tube shows that the discharge is accompanied by luminosity at those parts of the tube at which the graph is concave to the axis, and at no others. There are also, as Thomson points out (*l. c. ante*, p. 267), theoretical reasons which lead us to suppose that luminosity is accompanied by concavity of the graph.

Thus the graph at which Thomson arrives, being convex at every point, precludes the possibility of luminosity in any part of the tube ; it shows the distribution of electric force in a non-luminous discharge.

Further, it is well-known that under suitable conditions the gas in a discharge-tube presents a striated appearance, light and dark bands occurring alternately and at regular intervals, except in the neighbourhood of the electrodes. Thomson has obtained a discharge through a tube fifty feet in length, and observed that the whole tube, with the exception of a few inches near the cathode, was filled with these striations.

It appears therefore as if the true system of electrical equations, account being taken of the volume equations only, without reference to the boundary conditions, ought to lead to an infinite system of striations ; in fact, the graph for  $y$  should be a regular succession of waves, and  $y$  itself a periodic function of  $x$ .

It must be borne in mind that Thomson's graph is only one out of an infinite series of curves, all of which are represented by the same differential equations, and this leads us to consider firstly, whether any other member of this family of curves bears any resemblance to Graham's experimental curve ; and, secondly, whether any member can consist of a series of regular waves, and so correspond to a periodic solution.

Now it will appear in the course of the present paper that there is considerable probability that both of these questions must be answered in the negative. If this is so, it follows that the complete explanation cannot be implicitly contained in Thomson's differential equation ; in order to arrive at it,

new physical considerations will have to be introduced, which were not allowed for in forming this equation.

§ 2. Our analysis seems to indicate that there is only one explanation possible which is consistent with the main facts of the theory of conduction by ions, and this, stated briefly, is somewhat as follows :—

Thomson's equation gives a solution for the case of steady motion which not only is mathematically possible, but is the only solution which satisfies the assumed conditions throughout. This steady motion, however, is, under certain circumstances, unstable, just as the steady motion to which the hydrodynamical equations lead for the case of liquid flowing through an orifice is unstable. And, just as the liquid is known in nature to break up into a succession of small drops, so the discharge in a vacuum-tube breaks up, under suitable conditions, into a succession of small discharges, each discharge forming a single striation.

A mathematical explanation of this may be given in the following way :—

If we suppose that Thomson's equations are absolutely true over all ranges of the variables, then there is only one form of discharge possible, and this is non-luminous. When, however, the volume-density of the ions becomes indefinitely great, it is obvious that these equations can no longer hold without modification. It is impossible to get an infinite volume-density of electricity in nature, and this fact is not contained in the equations. We are therefore compelled to admit the existence of new forces which were not allowed for in the original equations ; *these forces are negligible until the volume-density of the ions reaches a certain large limit, but they then come into action, and are sufficient to prevent the volume-density from ever actually becoming infinite.* These forces may be of the nature of a repulsion between pairs of ions which have approached indefinitely near to each other, or, if we imagine the ions to be bodies of finite size, they will consist of the forces of elasticity which prevent a collection of such bodies from being compressed into an indefinitely small space.

But, without making any assumptions about the nature of these forces beyond those laid down in the sentence in italics, it can be shown that the existence of such forces makes possible a second type of solution, which is essentially different from that considered by Thomson, and that this solution, interpreted physically, predicts the existence of a system of striations in the middle of the tube, which may be expected

to give place to other phenomena in the region of the electrodes.

§ 3. The present section consists of an explanation of the notation to be used, and a summary of those parts of Thomson's paper which are essential to the theory. We are considering a discharge in perfectly pure gas, between two parallel and infinite plates.

Let  $x$  be a coordinate measured along the line of discharge, the positive axis of  $x$  being drawn from the anode to the cathode. The electrical intensity at any point will be denoted by  $X$ . The positive and negative ions are supposed to move in opposite directions with velocities proportional to  $X$  (Thomson, *l. c. ante*, p. 253). These velocities will be denoted by  $k_1 X$  and  $k_2 X$  respectively, the former being parallel to the positive axis of  $x$ . The number of positive ions per unit volume is  $n_1$ , and of negative ions  $n_2$ . Of these a certain number recombine, and this number is supposed to be  $\alpha n_1 n_2$ , since, other things being equal, it will be proportional to the product  $n_1 n_2$ . In the same unit volume, a certain number of molecules become dissociated, and these produce  $q$  ions of each sort per unit time.

No assumption is as yet made as to the way in which  $q$  and  $\alpha$  depend on other quantities; but from their definition they must be positive quantities at every point of the line of discharge,

If  $e$  be the charge carried by each ion, the fundamental equations for the case of steady motion are

$$\frac{dX}{dx} = 4\pi e(n_1 - n_2), \dots \dots \dots \quad (1)$$

$$\frac{d}{dx}(k_1 n_1 X) = q - \alpha n_1 n_2, \dots \dots \dots \quad (2)$$

$$-\frac{d}{dx}(k_2 n_2 X) = q - \alpha n_1 n_2. \dots \dots \dots \quad (3)$$

Of these the first is the fundamental equation of electrostatics; the two others contain the fact that the number of ions of either kind in a fixed element of volume remains constant; they are therefore the mathematical expression of the fact that the motion is steady.

From equations (2) and (3) it appears that  $(k_1 n_1 + k_2 n_2)X$  is independent of  $x$ , and its value is easily seen to be  $i/e$ , where  $i$  is the current across any unit area perpendicular to the axis. Thus

$$(k_1 n_1 + k_2 n_2)Xe = i. \dots \dots \dots \quad (4)$$

Solving equations (1) and (4) for  $n_1$  and  $n_2$ , we have

$$n_1 e = \frac{1}{k_1 + k_2} \left\{ \frac{i}{X} + \frac{k_2}{4\pi} \frac{dX}{dx} \right\}, \dots \quad (5)$$

$$n_2 e = \frac{1}{k_1 + k_2} \left\{ \frac{i}{X} - \frac{k_1}{4\pi} \frac{dX}{dx} \right\}; \dots \quad (6)$$

and the substitution of these values in either of the remaining equations gives

$$\begin{aligned} & \frac{1}{4\pi e} \frac{k_1 k_2}{k_1 + k_2} \frac{d}{dx} \left( X \frac{dX}{dx} \right) \\ &= q - \frac{\alpha}{X^2 e^2 (k_1 + k_2)^2} \left( i + \frac{k_2}{4\pi} X \frac{dX}{dx} \right) \left( i - \frac{k_1}{4\pi} X \frac{dX}{dx} \right). \end{aligned} \quad (7)$$

Writing  $2y$  for  $X^2$  and  $p$  for  $\frac{dy}{dx}$ , this becomes

$$\frac{1}{4\pi e} \frac{k_1 k_2}{k_1 + k_2} \frac{d^2 y}{dx^2} = q - \frac{\alpha}{2ye^2 (k_1 + k_2)^2} \left( i + \frac{k_2}{4\pi} p \right) \left( i - \frac{k_1}{4\pi} p \right), \quad (8)$$

and this is Thomson's equation for  $y$ .

The boundary conditions are taken to be

$$n_1 = 0$$

at the anode, and

$$n_2 = 0$$

at the cathode.

For, considering any small element of volume  $dx$ , terminated in one direction by the anode, it is clear that no positive ions can occur inside this element except those which have actually been produced by dissociation inside it. Now positive ions are produced at a rate  $qd\lambda$ , and the average time during which each ion remains in this element after its production is of the same order of quantities as  $\frac{dx}{k_1 X}$ . Thus the total number of positive ions in a length  $dx$  measured from the anode is of the order of  $(dx)^2$ , so that at the anode  $n_1 = 0$ .

Similarly,  $n_2 = 0$  at the cathode.

§ 4. With a view to simplifying the discussion of the differential equation, an assumption will now be made to the effect that the quantities  $q$  and  $\alpha$  depend only on the electric force at the point at which they are measured. It will be seen in a subsequent section that there is very little probability that this assumption is a legitimate one; but in the same section I shall endeavour to show that the limitations caused by its introduction can easily be removed.

In virtue of this assumption  $q$  and  $\alpha$  will now be single-valued functions of  $y$ , and they must, as has already been noticed, be positive for all values of  $y$ .

If  $\frac{d^2y}{dx^2}$  is replaced by  $p \frac{dp}{dy}$ , equation (8) will reduce to an equation which involves  $p$  and  $y$  only, and which may be written

$$\frac{1}{4\pi e} \frac{k_1 k_2}{k_1 + k_2} p \frac{dp}{dy} = q + \frac{\alpha k_1 k_2}{32\pi^2 e^2 (k_1 + k_2)^2 y} \left( p^2 - 4\pi i \left( \frac{1}{k_1} - \frac{1}{k_2} \right) p - \frac{16\pi^2 i^2}{k_1 k_2} \right). \quad (9)$$

Taking  $p$  and  $y$  as coordinates, a graph may be constructed showing the relation between  $p$  and  $y$  which is implied by the above equation, and this graph will consist of a singly-infinite system of curves.

Since  $y, n_1, n_2$  must all be positive, the only parts of this graph which are of any importance in connexion with the present problem lie in that part of the  $p, y$  plane which is bounded by the two lines  $p = \frac{4\pi i}{k_1}$  and  $p = -\frac{4\pi i}{k_2}$ , and is on the positive side of the axis of  $p$ .

For any given values of  $p$  and  $y$  equation (9) gives a single value for  $\frac{dp}{dy}$ , so that through every point in the  $p, y$  plane one, and only one, curve passes. An exception to this occurs at the intersections of the lines  $p = \frac{4\pi i}{k_1}$  and  $p = -\frac{4\pi i}{k_2}$  with the line  $y=0$ . At these two points  $\frac{dp}{dy}$  becomes indeterminate, and an infinite number of curves branch out from these points. Moreover, the axis of  $p$  satisfies equation (9) at every point, for at all points on it  $y=0$  and  $\frac{dp}{dy}=\infty$ . This line is therefore a curve of the system, and hence no other curve can meet this axis except in the two singular points mentioned above.

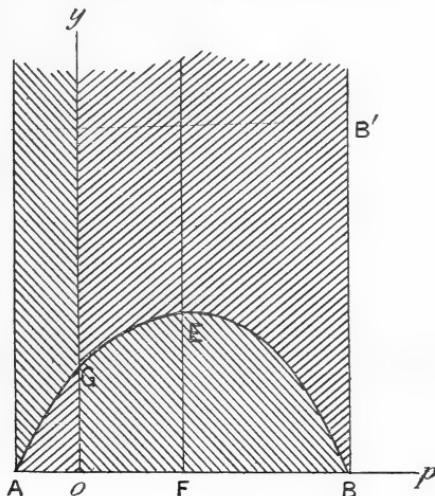
The points on the system of curves at which  $\frac{dp}{dy}=0$  are, by equation (9), given by

$$\left\{ p - 2\pi i \left( \frac{1}{k_1} - \frac{1}{k_2} \right) \right\}^2 = 4\pi^2 i^2 \left( \frac{1}{k_1} + \frac{1}{k_2} \right)^2 - \frac{32\pi^2 e^2 (k_1 + k_2) q y}{\alpha k_1 k_2}. \quad (10)$$

If the curve of which this is the equation be drawn in the plane of  $p, y$ , it will meet the curves of the graph in the points at which the tangents to the latter are parallel to the axis of  $y$ . This curve will in future be spoken of as the curve  $(\alpha)$ , and the two singular points in which the axis of  $p$  meets the lines  $p = \frac{4\pi i}{k_1}$  and  $p = -\frac{4\pi i}{k_2}$  will be denoted by A and B. It is clear that the curve  $(\alpha)$  passes through the two points A and B.

§ 5. In the simplest case, in which  $q$  and  $\alpha$  are constants, this curve is a parabola whose axis is parallel to the axis of  $y$ , and whose concavity is turned downwards (fig. 1). Considering only those parts of the plane for which  $p$  is positive, equation (9) shows that for curves of the original system  $\frac{dp}{dy}$  is positive at all points outside the parabola, and negative at all points inside ; the reverse is true when  $p$  is negative.

Fig. 1.



Hence in fig. 1 the value of  $\frac{dp}{dy}$  at any point must have the same sign as the value of  $\frac{dp}{dy}$  for a point moving in the direction indicated by the lines of the shading at that point. Every curve of the system cuts the line  $p=0$  at right angles, for at points on this line  $\frac{dy}{dx}=0$ , and therefore  $y$  passes through a maximum or minimum value.

These considerations enable us to form some idea of the disposition of the curves in that part of the plane of  $p, y$  with which we are concerned.

Any curve starting from A and meeting OG (fig. 1) must clearly be an arched curve terminating in B. For the conditions already laid down prevent it from meeting either the line OB or arc GEB of the parabola, or again from bending back and recrossing OG. The limiting curves of this system are on the one hand the axis of  $p$ , and on the other hand the curve which actually passes through G. At no point on any curve of this system can  $y$  reach a value greater than OG;  $y$ , therefore, is always less than a critical value,  $y_0$ , given by

$$y_0 = OG = \frac{i^2 \alpha}{2qe^2(k_1 + k_2)^2} \dots \dots \dots \quad (11)$$

There is a second system, consisting of curves which pass through A but do not meet OG. These must therefore meet AG, be bent away from the axis of  $y$  after crossing AG, and finally meet AA'.

It can be shown that these curves cannot attain to an infinite value of  $y$  before meeting the line AA'. For we can find the shape of the curves which fill up that part of the  $p, y$  plane which lies between the lines AA' and BB', and for which  $y$  is infinite. The differential equation of these curves is seen by equation (9) to be

$$\frac{1}{4\pi e} \frac{k_1 k_2}{k_1 + k_2} p \frac{dp}{dy} = q,$$

and this represents a system of parabolas which are convex to the axis of  $p$ . Since these parabolas cannot be members of that system of curves which we are now discussing, we conclude that there must be some point A', in the line AA', beyond which this system never reaches. As the curves of a system cannot cross one another, it must be the curve that actually passes through G which reaches this limiting point A'.

There is therefore a maximum limit to the value of  $y$  on curves of the second class, and this is given by

$$y_1 = AA'.$$

There is an exactly similar system of curves passing through B and meeting BG. For this system also there is a maximum limit to the value of  $y$ , given by

$$y_2 = BB'.$$

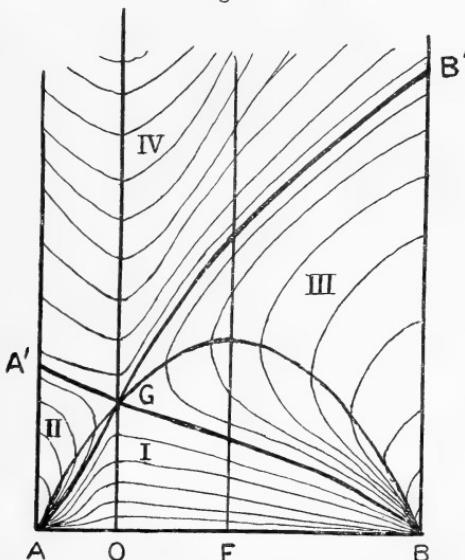
The system of curves which pass through B, and do not meet BG, must consist of the curves which meet OG. This

system is therefore identical with the first system which we considered, namely, the series of arches which join the points A, B.

The remainder of the part of the  $p, y$  plane with which we are dealing is filled up by a system of curves which meet OG above G, each curve having its lowest point on OG. For curves of this type there is an inferior limit to the value of  $y$ , and this is the value  $y_0$  already found in equation (11).

The curves in the  $p, y$  plane are thus seen to fall into four classes. These are represented in their essential features by

Fig. 2.



the curves in fig. 2, and the four classes will in future be referred to by the numbers in this diagram.

The limiting curves are the two curves  $AGB'$ ,  $A'GB$ , which are drawn in thick lines in the diagram. These curves intersect in G and divide the plane into four regions, in each of which lie all the curves in one of the four classes.

§ 6. Let us now examine to what extent the arrangement of curves found in the last section will be altered if we replace the assumption that  $q$  and  $\alpha$  are constant by the more general assumption that they are positive quantities which vary with  $y$ .

From the equations of § 4, it follows at once that :

(i.) The curve ( $\alpha$ ) is no longer a parabola, but is still a curve which passes through the points A and B, and is symmetrical about the same axis as before.

(ii.) At all points adjacent to the line  $y=0$ , the sign to be given to  $\frac{dp}{dy}$  in drawing the system of curves remains the same as before. The same is true for points at which  $y$  is infinite.

(iii.) Hence, since  $\frac{dp}{dy}$  must change sign in crossing either the curve  $(\alpha)$  or the axis of  $y$ , it follows that the curve  $(\alpha)$  must cross the positive axis of  $y$  an odd number of times.

(iv.) The curve  $(\alpha)$  cannot meet the lines  $AA'$ ,  $BB'$  in any points except A and B.

From this we deduce that the new curve  $(\alpha)$  consists primarily of an arch through A and B, and secondly, of any number of closed curves either inside or outside the arch.

If, then, a shaded diagram is drawn similar to fig. 2, the directions of the shading adjacent to the arch through AB, as also the direction of the shading at infinity, must remain unaltered.

The four types of curves of which the existence has already been discovered will therefore continue to exist in the new graph in the  $p, y$  plane. The general appearance of the new graph will, however, depend on whether the curve  $(\alpha)$  cuts the axis of  $y$  once or more than once.

For the effect of introducing into this locus new closed curves which do not meet the axis of  $y$ , is simply a twisting of the lines already in the graph, and this introduces no essentially different type of curve. But the effect of admitting into this locus new closed curves which do cut the axis of  $y$ , or of allowing the original arch to meet this axis more than once, will be the introduction of an entirely new type of curve into the  $p, y$  graph, and this will consist of a series of closed curves. Fig. 3 will, I hope, make the truth of these statements clearer\*.

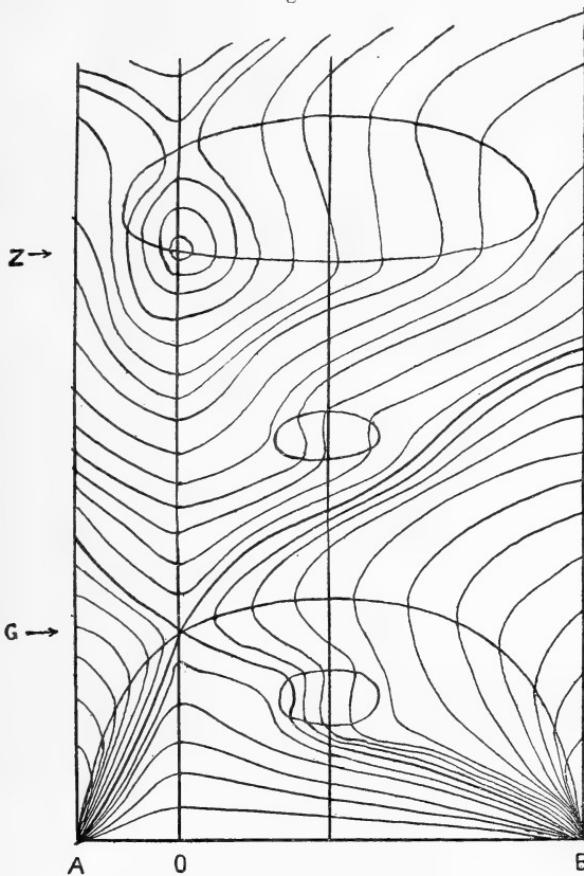
§ 7. The presence of closed curves in the  $p, y$  graph immediately makes possible a periodic solution of the original equation. For as we pass round such a curve time after time the same values of  $p$  and  $y$  recur indefinitely; so that the graph of  $y$  in terms of  $x$  will be a regular succession of waves and furrows.

A solution of this type, interpreted physically, would give a striated solution as regards the middle of the tube; but the whole solution breaks down when we attempt to satisfy the

\* The three closed curves which are symmetrical about the central axis, together with the arch through AB, constitute the curve  $(\alpha)$ . The closed curves in the  $p, y$  graph are seen surrounding the point Z on the axis of  $y$ .

terminal conditions. To satisfy these, the closed curve would have to meet the lines  $AA'$ ,  $BB'$ . Now if it crosses either of these lines it cannot give a solution at all, and if it is to touch either of them the curve ( $\alpha$ ) must pass through the point of contact, and this has been seen to be impossible.

Fig. 3.



It might, however, be urged that near the electrodes the volume-equations of § 3 give place to other and different volume-equations ; and if this were so, there is nothing to prevent all the conditions of the problem from being satisfied.

Under these circumstances, the examination of whether closed curves can or can not occur in the  $p, y$  graph becomes a matter of importance. The necessary and sufficient condition that closed curves shall be an impossibility is that the curve ( $\alpha$ ) shall only meet the axis of  $y$  in one point, and this condition will in future be spoken of as condition A.

We have seen that if condition A is fulfilled all the curves which constitute the  $p, y$  graph come under one or other of the four classes represented in fig. 2.

We shall in the following sections confine ourselves to the consideration of these four types of curves, and it will appear that if these four types alone exist, there is only one type of solution possible in addition to that already arrived at by Thomson.

Even if condition A is not satisfied this alternative type of solution will still be possible, but, as has already been pointed out, we are no longer justified in asserting that it is the only alternative. A second alternative becomes possible on assuming that the gas near the electrodes is in an abnormal state.

§ 8. From our knowledge of the graph in the  $p, y$  plane it is easy to deduce the corresponding graph in the plane of  $x, y$ . An intersection of a  $p, y$  curve with the axis of  $p$  will give rise to a maximum or minimum value for  $y$  on the corresponding  $x, y$  curve, and an intersection with the curve ( $\alpha$ ) will give rise to a point of inflexion. The new graph, in strictness, consists of a doubly infinite system of curves, but it will be sufficient to consider the system as singly infinite, a single curve corresponding to each curve in the  $p, y$  plane. A second infinity is then obtained by moving each curve parallel to itself along the axis of  $x$ .

The curves in the plane of  $x, y$  fall into four classes corresponding to the four classes of curves in the  $p, y$  plane.

The curves of the first class will each give rise to a single arch in the plane of  $x, y$ ; this arch stands on the axis of  $x$ , and is on the positive side of this axis. Since we are now considering the case in which  $q$  and  $\alpha$  are no longer constants, this arch may or may not have points of inflexion. Every curve of this system leaves the axis of  $x$  at an angle  $\tan^{-1}\left(\frac{4\pi i}{k_1}\right)$ , and meets it again at an angle  $\tan^{-1}\left(\frac{4\pi i}{k_2}\right)$ .

The limiting curves of this system are :—

(i.) An arch which shrinks to a point on the axis of  $x$ . This corresponds to the limiting curve AFB in fig. 2.

(ii.) An arch of infinite span which touches asymptotically the line  $y = y_0$  (see equation 11). This corresponds to the curve AGB in fig. 2, and  $y_0$  must now be defined as the smallest (or, if condition A is satisfied, the only) root of the equation

$$y = \frac{i^2 \alpha}{2qe^2(k_1 + k_2)^2} \cdot \cdot \cdot \cdot \cdot \quad (12)$$

The curves of the second class are single slant lines, which leave the axis of  $x$ , making with it an angle  $\tan^{-1}\left(\frac{4\pi i}{k_2}\right)$  in the negative direction. After passing through at least one point of inflexion the tangent again makes an angle  $\tan^{-1}\left(\frac{4\pi i}{k_2}\right)$  with the negative axis of  $x$ , and at this point, in so far as they are of interest in connexion with the present problem, they terminate abruptly. There is a superior limit  $y_1$  (see § 5) to the value of  $y$  at this point of termination.

The limiting curves of this class are :—

(i.) An indefinitely short straight line close to the axis of  $x$ , and making with it an angle  $\tan^{-1}\left(\frac{4\pi i}{k_2}\right)$ .

(ii.) A curve which approaches the line  $y=y_0$  asymptotically, has a point of inflexion on this line, and again recedes from it asymptotically. The length on both sides of the point of inflexion is therefore infinite.

There is no difference between curves of the third class and those of the second, except that the slant is in the opposite direction, and that  $\frac{4\pi i}{k_1}$  must now be substituted for  $\frac{4\pi i}{k_2}$ . There is again a superior limit  $y_2$  to the value of  $y$ .

Curves of the fourth class are inverted arches, which terminate abruptly in two points  $\alpha, \beta$ . At  $\alpha$  the tangent makes an angle  $\tan^{-1}\left(\frac{4\pi i}{k_2}\right)$  with the negative axis of  $x$ , and after the value of  $y$  has passed through some minimum  $\chi$ , the curve terminates in  $\beta$ , at which point its tangent makes an angle  $\tan^{-1}\left(\frac{4\pi i}{k_1}\right)$  with the positive axis of  $x$ . The value of  $y$  at  $\alpha$  has an inferior limit  $y_1$  (see p. 252), and the value at  $\beta$  an inferior limit  $y_2$ . Also  $\chi$  has an inferior limit,  $y_0$  (equation 12).

The limiting curves are :—

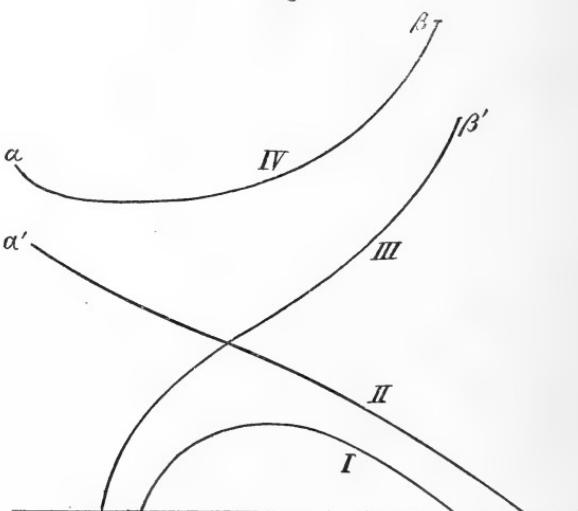
(i.) A curve which approaches  $y=y_0$  asymptotically in both directions.

(ii.) A finite arc of a parabola, at every point of which  $y$  is infinite, the latus rectum of the parabola being finite (see p. 252).

A curve of each of the four classes is shown in fig. 4. The dotted lines show the three critical values for  $y$ , which have been denoted by  $y_0, y_1, y_2$ .

At an anode the terminal condition has been seen to be  $n_1=0$  or  $\frac{dy}{dx} = -\frac{4\pi i}{k_2}$ . It is therefore possible for an anode to be at a point such as  $\alpha$  or  $\alpha'$  in fig. 4, but nowhere else.

Fig. 4.



And similarly a cathode can only exist at a point such as  $\beta$  or  $\beta'$ . If then it is possible to satisfy the condition for an anode and the condition for a cathode at two points on the same curve, that curve must be of the fourth class.

§ 9. The question which now suggests itself is the following:— If we plot out the actual graph for  $y$  along any discharge, does the curve so obtained necessarily coincide with a single curve of the infinite series typified in fig. 4?

If this question must be answered in the affirmative, the graph must, as we have seen in the last section, be a curve of the fourth class, terminated by the points  $\alpha$  and  $\beta$ . This is in fact the only solution which satisfies equation (8) at every point, satisfies the assumed boundary conditions at the electrodes, and makes  $n_1$ ,  $n_2$ , and  $y$  positive at every point. It is a solution of this type that is arrived at in Thomson's paper.

The only alternative to this solution would lie in making up a graph discontinuously out of a number of the curves or parts of curves shown in fig. 4. We are therefore led to inquire whether it is ever possible to pass from one curve to another without violating physical conditions of continuity.

Since the velocity of the ions must be continuous,  $x$ , and

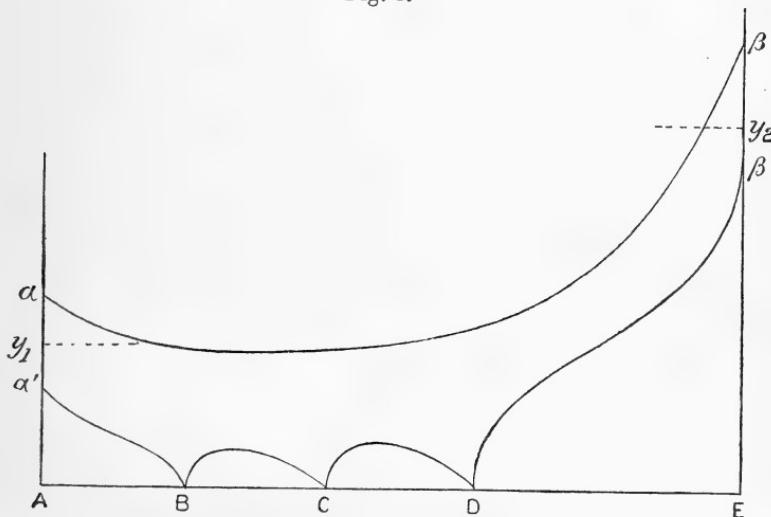
therefore  $y$ , must be continuous. If we suppose that  $p$  also is to be continuous we are reduced to keeping on the same curve, for two curves can never touch each other, since by equation (8) the curvature depends only on  $y$  and  $p$ .

The effect of making  $p$  discontinuous is to make  $\frac{d^2y}{dx^2}$  become infinite. If, then, equation (8) is not to be violated,  $y$  must be zero at that point.

An alternative solution can therefore be obtained by building up the graph of  $y$  out of pieces from the curves in fig. 4, care being taken to only pass from one curve to another on the axis. The solution so obtained is such that the electric force and velocities of the ions are continuous, and it satisfies all the mathematical equations.

It is, moreover, obvious that there is only one type of solution of this kind possible. This consists of any number of arched curves of the first class placed end to end and terminated by a curve of the second class at the anode, and a curve of the third class at the cathode; the points  $\alpha'$  and  $\beta'$  of these curves (fig. 4) being the anode and cathode respectively.

Fig. 5.



A solution of each of the two types that have been found to be mathematically possible is shown in fig. 5.

§ 10. When we attempt to interpret this second solution, we are immediately confronted with the fact that it is impossible, for physical reasons, that  $y$  should vanish. At a point such

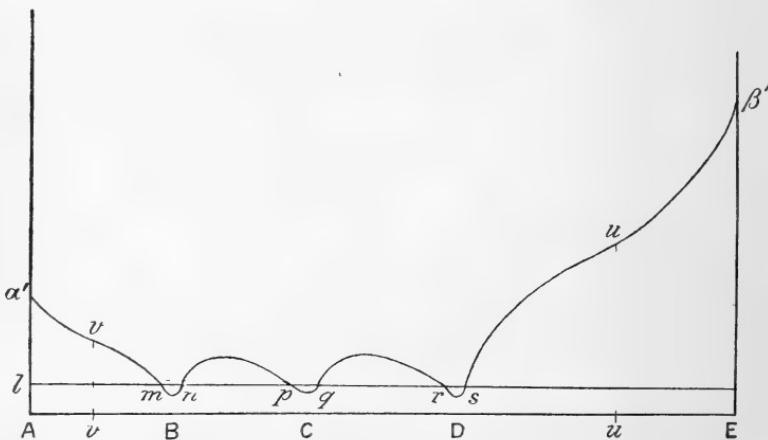
as B, C, or D in fig. 5, we should not only have an infinite volume-density of ions, but also all the ions would be at rest.

It has, however, been already pointed out (§ 2) that as  $y$  becomes indefinitely small, the equation from which our solution has been derived ceases to hold. New forces come into play, with the result that the graph representing the actual values of  $y$  ceases any longer to satisfy the differential equation which holds elsewhere. And if these forces are forces which prevent the volume-density of ions from becoming infinite (as must be the case if the ions are of finite size), the change in the differential equation will be of such a nature as to prevent the graph from ever meeting the axis.

Let us imagine that  $\eta$  is some small value of  $y$ , such that these forces do not produce any effect till  $y$  falls below a certain value  $\eta$ , but that for values of  $y$  less than  $\eta$  the equations of § 3 cease to hold.

In fig. 6 let A be the anode, A B C D E the axis along which  $y=0$ , l m n . . . the line  $y=\eta$ .

Fig. 6.



Starting from the point  $\alpha'$  in the anode, such that the value of  $y$  is less than the critical value  $y_1$ , let the graph be drawn as in fig. 5 until it meets the line  $y=\eta$  in some point  $m$ . And after the graph has reached this line, let it be continued so as to satisfy the true differential equation which holds when  $y$  is less than  $\eta$ .

The graph must either remain in the region in which  $y$  is less than  $\eta$ , or else emerge from this region at some point  $n$  in  $l m n \dots$ . If in the limit we assume  $\eta$  to be very small, the former alternative need not be considered. Beyond  $n$

the graph satisfies the known differential equation ; it is therefore an arch of the type occurring in fig. 5 ; and since both  $p$  and  $y$  are already determined at the point  $n$  which is not on the axis  $y=0$ , this arch is completely determined by the part of the graph already drawn. This arch again enters the region in which  $y$  is less than  $\eta$  at some point  $v$ , and so on, until it finally emerges at some point  $s$ , and takes the shape of a line similar to  $D\beta'$  in fig. 6. The point  $\beta'$  on this curve at which the graph satisfies the condition for a cathode may be taken for the actual cathode, and in this case the graph we have arrived at will satisfy the appropriate terminal conditions at each electrode.

The graph so obtained also satisfies the true physical equations at every point. For so long as  $y$  is greater than  $\eta$  it satisfies the mathematical equations, with which the physical equations are supposed to coincide, and in the region for which  $y$  is less than  $\eta$  it must, from the way in which it has been constructed, satisfy the physical equations.

Further, the smaller  $\eta$  becomes, the more closely will this graph approach to the known graph in fig. 5, so that if  $\eta$  be sufficiently small, the graph in fig. 5 may be supposed to represent the real graph if we allow for the existence of the disturbing forces by rounding off the corners B, C, D.

This effect of disturbing forces finds a parallel in almost every branch of physics. Consider, for example, liquid flowing along the edge of an obstacle. Let us draw a graph giving the reciprocal of the velocity of the fluid at the various points of the edge, the velocity being determined by the hydrodynamical equations for the motion of a non-viscous incompressible fluid. At a point of the graph corresponding to a sharp corner on the obstacle there will be a cusp on the axis exactly similar to the points B, C, D in fig. 5, showing that the theoretical velocity at these points is infinite. In the actual flow the velocity is not infinite on account of the viscosity of the fluid, and the effect on the graph of this disturbing influence is therefore a "rounding-off" of sharp corners.

§ 11. We are now in a position to give a physical interpretation of the solution which is represented by the graph in fig. 6.

As is well known, both theory and experiment show that light may be expected to appear at points for which  $q - \alpha n_1 n_2$  is negative; that is to say, wherever the number of ions that recombine is greater than the number produced by dissociation. Equation (8) shows that  $q - \alpha n_1 n_2$  is negative or positive

according to whether  $\frac{d^2y}{dx^2}$  is negative or positive. Luminescence may accordingly be expected whenever the graph is concave to the axis, and darkness where it is convex\*.

In fig. 6 let  $u$ ,  $v$  be the points of inflexion which are known to exist in  $D\beta'$ ,  $\alpha'B$ .

Then from  $\beta'$  to  $u$  the curve is convex to the axis, and therefore we expect darkness—the Crookes's dark space.

From  $u$  to  $s$  the curve is concave, and therefore we expect luminosity—the negative glow.

Beyond  $s$  we expect alternations of light and darkness—the striae—until we come to the neighbourhood of the anode, and here the solution leads us to expect phenomena similar to those occurring at the cathode.

What happens in nature is that the appearances presented at the anode vary greatly in different discharges, and, in general, bear very little resemblance to those observed at the cathode. This appears, at first, to be in opposition to our theory, but I hope in the second part of this paper to show that, so far from being in opposition to the theory, it becomes a logical consequence of the theory as soon as we introduce the supposition that the velocity of the negative ions is much greater than that of the positive.

**XXI. *On the Coincidence of Refracted Rays of Light in Crystalline Media.*** By LOUIS TRENCHARD MORE, Ph.D., *Adjunct-Professor of Physics in the University of Nebraska*†.

IT is very generally assumed in treatises on optics that rays of light in doubly-refracting media break up into two parts, unless the light traverses a path coinciding with an optic axis of the crystal, or unless the path coincides with the major or minor axis of the elliptic section of the wave-surface. In the former case, both the velocities and the directions of the rays coincide; in the latter, although the velocities are different, the paths are the same. That these are but two special cases of an infinite number in which the paths of the ordinary and extraordinary rays coincide was first shown by Dr. D. B. Brace‡. The reason that this phenomenon has hitherto escaped experimenters is probably because, under these conditions, the angle of refraction of the rays is, in general, either so large that it is greater than the critical

\* J. J. Thomson, Phil. Mag. xlvi. p. 267 (1899).

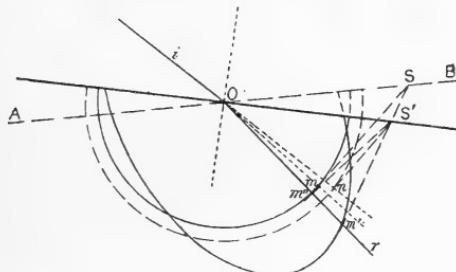
† Communicated by the Author. Read in part to the American Mathematical Society, August 1899.

‡ Wied. Ann. Bd. xxvi. p. 576.

angle of the crystal, unless it is immersed in a very highly refracting medium, or else it is so small that it nearly coincides with an axis of the elliptic wave-front.

The geometrical construction for obtaining the coincidence of the two rays is simple, and follows at once from Huyghens' principle. Let, in fig. 1, the ellipse and circle represent a principal section of Fresnel's wave-surface, and let AOB be

Fig. 1.



the surface of a crystal. - If  $Om$  is an ordinary ray, we find the corresponding extraordinary ray  $Om'$  by drawing a tangent to the circle at  $m$  and, from where it cuts the surface at  $S$ , a tangent to the ellipse at  $m'$ . But if it is assumed that the two rays are to coincide, say in the line  $Om'$ , then tangents drawn from the intersections of this line with the circle at  $m''$  and with the ellipse at  $m'$  will meet in some point  $S'$ . Evidently, if  $S'$  be connected with  $O$  as a new surface of the crystal, all the conditions of Huyghens' principle are satisfied. To obtain the ray in the bounding medium a circle of proper radius  $On$  is drawn ; a tangent from  $S'$  to  $n$  gives the direction of this incident ray  $On$ .

If, then,  $OS'$  is the surface of a crystal, an incident ray  $iO$  will traverse the crystal undivided in direction along the line  $Or$ , and the angle of refraction will obey the simple sine law. The locus of the points  $S'$  gives all possible solutions of the problem.

Figs. 2-6 show this locus for the three principal sections of a biaxal crystal and for both a negative and a positive uniaxial crystal. The curves are symmetrical about both axes and are of the eighth degree. There are two sets : the full lines being found by drawing tangents on the same side of the centre, and the dotted curves by tangents from opposite sides. For the uniaxial crystal a branch of the curve becomes a pair of straight lines perpendicular to the optic axis. The dotted curves are only approximately correct and are drawn, for convenience, much closer to the centre of the figure than

Fig. 2.

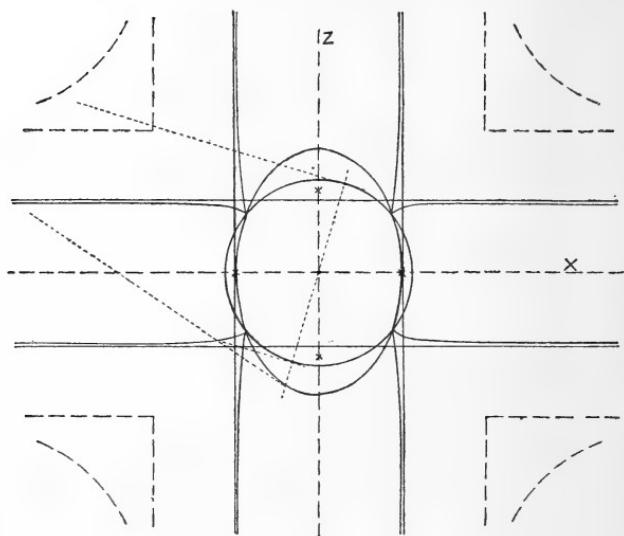
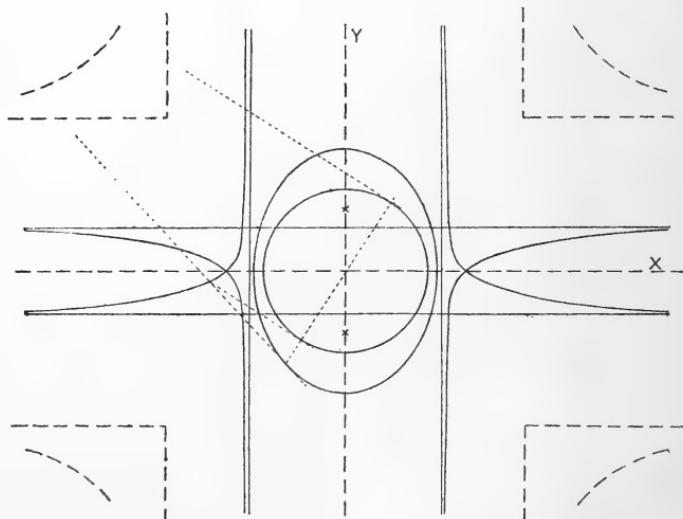


Fig. 3.



they should be. Unless otherwise stated, they will be omitted from the future discussion of the problem.

The analytical discussion has been limited to the properties of the locus in the three principal planes of the crystal. Let X be the axis of greatest elasticity, Y of mean, and Z of the least elasticity; and let  $a, b, c$  be the velocities of light along these three axes respectively: then  $a > b > c$ . If  $x', y', z'$  and  $x'', y'', z''$  are the intersections of two *radii vectores* with the two sheets of Fresnel's wave-surface,  $F=0$ , tangents at these points are expressed by the equations

$$(x-x') \frac{\partial F'}{\partial x'} + (y-y') \frac{\partial F'}{\partial y'} + (z-z') \frac{\partial F'}{\partial z'} = 0,$$

$$(x-x'') \frac{\partial F''}{\partial x''} + (y-y'') \frac{\partial F''}{\partial y''} + (z-z'') \frac{\partial F''}{\partial z''} = 0.$$

Then the locus,  $F=0$ , of the intersections of these tangents is the required envelope. Using the section in the plane XZ we have the following equations :—

$$\frac{x'}{x''} = \frac{z'}{z''},$$

since the two vectors are assumed to coincide; also the equations of the circle and the ellipse,

$$x'^2 + z'^2 = b^2,$$

$$a^2 x''^2 + c^2 z''^2 = a^2 c^2;$$

lastly tangents to these

$$xx' + zz' = b^2,$$

$$a^2 xx'' + c^2 zz'' = a^2 c^2.$$

Changing to polar coordinates, where  $b$  and  $\rho$  are the lengths of the vectors and  $\alpha$  the angle with the axis X, then

$$\rho^2 = \frac{a^2 c^2}{a^2 \cos^2 \alpha + c^2 \sin^2 \alpha} = \frac{(a^2 c^2)^2}{(a^2 x \cos \alpha + c^2 z \sin \alpha)^2},$$

$$x \cos \alpha + z \sin \alpha = b,$$

$$\cos^2 \alpha + \sin^2 \alpha = 1.$$

By elimination of  $\alpha$  and arrangement of terms, the equation of the envelope may be written in the following form :—

$$(a) \dots c^4(x^2 - b^2)(z^2 - a^2) - a^4(x^2 - c^2)(z^2 - b^2) \quad [(\text{fig. 2})]$$

$$+ 2acxz \sqrt{\{c^2(z^2 - a^2) - a^2(z^2 - b^2)\} \{c^2(x^2 - b^2) - a^2(x^2 - c^2)\}} = 0$$

The equation is of the eighth degree and symmetrical about the axes. By a permutation of the letters the cases where the circle is wholly in the ellipse and where the ellipse is wholly in the circle are at once obtained :

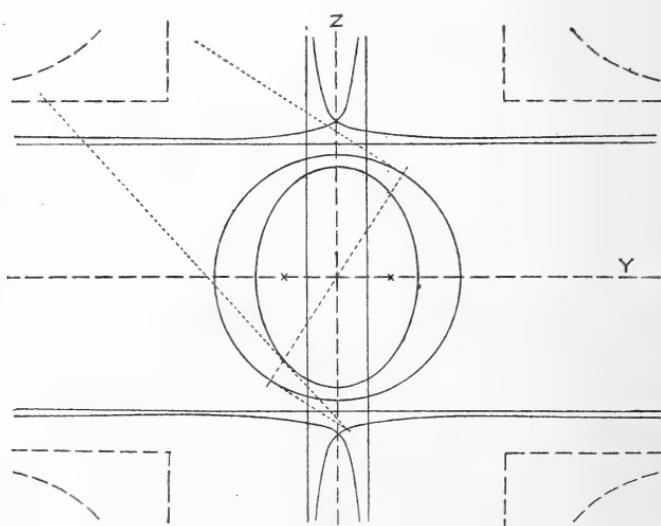
$$b^4(x^2 - c^2)(y^2 - a^2) - a^4(x^2 - b^2)(y^2 - c^2) \quad [(\text{fig. 3})]$$

$$+ 2abxy \sqrt{\{b^2(y^2 - a^2) - a^2(y^2 - c^2)\} \{b^2(x^2 - c^2) - a^2(x^2 - b^2)\}} = 0$$

$$c^4(z^2 - b^2)(y^2 - a^2) - b^4(y^2 - c^2)(z^2 - a^2) \quad [(\text{fig. 4})]$$

$$+ 2bcyz \sqrt{\{c^2(z^2 - b^2) - b^2(z^2 - a^2)\} \{c^2(y^2 - a^2) - b^2(y^2 - c^2)\}} = 0$$

Fig. 4.



To obtain the locus for a negative uniaxial crystal,  $b$  is equated with  $c$  in equation (a), giving

$$(x^2 - b^2) \{1/z^2 - (1/a^2 + 1/b^2 + 2/ab \sqrt{x^2/b^2 - 1})\} = 0.$$

The locus thus breaks up into two parts, a curve of the sixth degree and a pair of straight lines, at the extremities of the diameter  $b$  and perpendicular to the axis X, shown in figs. 5 and 6.

Fig. 5.

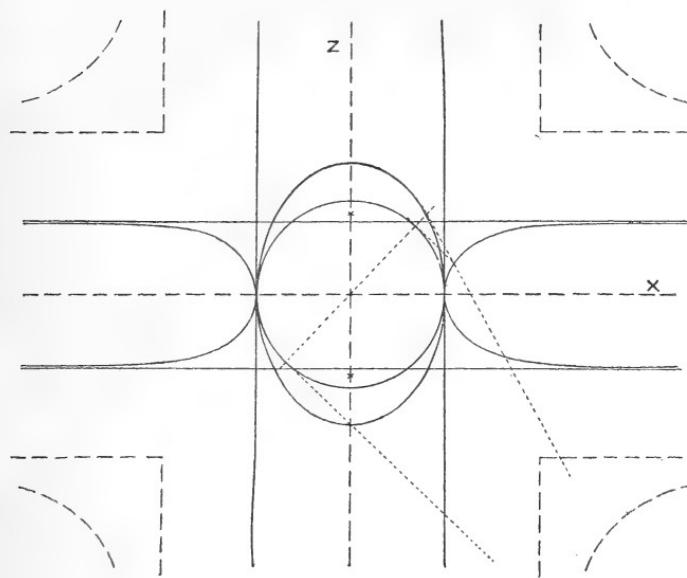
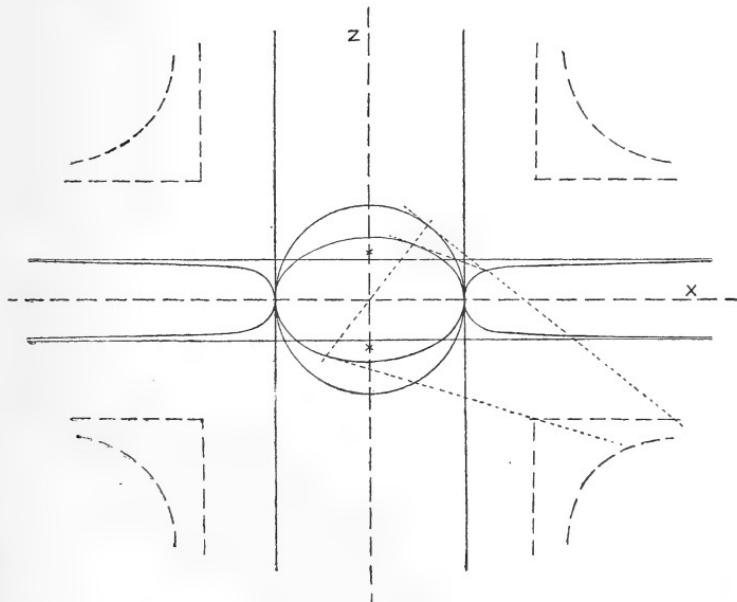


Fig. 6.



Returning to the general equation (*a*), it may for more convenient manipulation be put into the form of a quadric quadric,

$$z^4(\lambda_1 x^4 + \lambda_2 x^2 + \lambda_3) + 2z^2(\mu_1 x^4 + \mu_2 x^2 + \mu_3) + (\nu_1 x^4 + \nu_2 x^2 + \nu_3) = 0;$$

where

$$\lambda_1 = (a^2 - c^2)^4,$$

$$\lambda_2 = -2a^2(a^2 - c^2)^2(a^4 + b^2c^2),$$

$$\lambda_3 = c^4(a^4 - b^2c^2)^2,$$

$$\mu_1 = -a^2(a^2 - c^2)^2(a^2b^2 + c^4),$$

$$\mu_2 = \{2a^2b^2c^2(a^6 + c^6) - a^4c^4(a^2 + b^2)(b^2 + c^2) - 2a^4c^4(a^2 - b^2)(b^2 - c^2)\},$$

$$\mu_3 = -a^2b^2c^4(a^4 - b^2c^2)(a^2 - c^2) = -\sqrt{\lambda_3\nu_3},$$

$$\nu_1 = a^4(a^2b^2 - c^4)^2,$$

$$\nu_2 = -2a^4b^2c^2(a^2 - c^2)(a^2b^2 - c^4) = -2\sqrt{\nu_1\nu_3},$$

$$\nu_3 = a^4b^4c^4(a^2 - c^2)^2.$$

The asymptotes parallel to the axes are the roots of

$$\lambda_1 x^4 + \lambda_2 x^2 + \lambda_3 = 0,$$

$$\lambda_1 z^4 + 2\mu_1 z^2 + \nu_1 = 0.$$

Those for a negative uniaxal crystal reduce to

$$x = \pm b \frac{a^2 + b^2}{a^2 - b^2},$$

$$z = \pm \frac{ab}{a \pm b}.$$

The locus of a crystal intersects the axes in the points which are the roots of

$$\nu_1 x^4 + \nu_2 x^2 + \nu_3 = 0,$$

$$\lambda_3 z^4 + 2\mu_3 z^2 + \nu_3 = 0.$$

Inspection of these coefficients shows that both equations are perfect squares. Substituting their values we have

$$x^2 = b^2c^2 \frac{a^2 - c^2}{a^2b^2 - c^4},$$

$$z^2 = a^2b^2 \frac{a^2 - c^2}{a^4 - b^2c^2};$$

for a uniaxal crystal,

$$x^2 = b^2,$$

$$z^2 = \frac{a^2 b^2}{a^2 + b^2}.$$

These points, since  $a > b > c$ , are essentially real, and there are in each case four intersections with the axes; two, at least, must be singular points, and if the curve of the locus does not cross an axis all four have this property. They and the asymptotes have been located approximately on the diagrams.

An examination of the figures shows that a line through the origin of coordinates may cut the locus in four pairs of points. Since this line forms the trace of the surface of the crystal with a coordinate plane, there are, at most, *three* directions in which the ordinary and extraordinary rays coincide for this single section. There are, of course, an infinite number of these sections. It should be noted that the two intersections with the horizontal branch on the right must be taken with the intersection with the vertical branch on the left, and *vice versa*. If the surface of the crystal is cut tangent to the horizontal branch of the locus, two directions of coincidence are possible; for greater angles, only one. With a uniaxal crystal one of these solutions is due to a ray along the optic axis. As biaxal crystals, generally, have two of their indices of refraction nearly equal in value, one branch of the locus approximates closely to a straight line; so one pair of coincident rays is found near the axis of the ellipse which is more nearly equal to the radius of the circle.

Hitherto we have discussed only the conditions for the coincidence of the two rays inside the crystal. To complete the investigation the direction of the corresponding incident ray in the bounding medium must be determined. Huyghens' principle gives at once the solution. A circle is drawn, shown dotted in fig. 1 (p. 263), whose radius is proportional to the velocity of light in the medium, and a tangent is drawn to it from the point  $S'$ . The ray is then perpendicular to the tangent. Let  $d$  be the radius of this circle,  $\theta$  the angle of incidence of a ray in the bounding medium, and  $\alpha$  the angle between the normal to the surface and the axis  $X$ . Then  $(\theta + \alpha)$  is the angle made by the ray and  $X$ , and if  $x, z$  are the coordinates of a point on the envelope,

$$x \cos \alpha + z \sin \alpha = 0.$$

$$x \cos (\alpha + \theta) + z \sin (\alpha + \theta) = d.$$

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A solution of these equations gives

$$z = d \frac{\cos \alpha}{\sin \theta}, \quad x = -d \frac{\sin \alpha}{\sin \theta}.$$

These values substituted in the equation of the envelope of the uniaxial crystal,

$$(x^2 - b^2) \left\{ 1/z^2 - \left( 1/a^2 + 1/b^2 + 2/ab \sqrt{\frac{x^2}{x^2 - b^2}} \right) \right\} = 0,$$

give

$$(b) \left( \frac{\sin^2 \alpha}{\sin^2 \theta} - \frac{1}{m_0^2} \right) \left\{ \frac{\sin^2 \theta}{\cos^2 \alpha} - \left( m_0^2 + m_\epsilon^2 + 2m_0 m_\epsilon \sqrt{\frac{m_0^2 \sin^2 \alpha}{m_0^2 \sin^2 \alpha - \sin^2 \theta}} \right) \right\} = 0,$$

where  $m_0 = d/b$  and  $m_\epsilon = d/a$ .

The first factor  $\sin \theta = \pm m_0 \sin \alpha$  is the equation which satisfies the condition of coincidence of rays along the optic axis. As  $\theta$  and  $\alpha$  are on opposite sides of the normal to the surface, the minus sign is the one to be used. The second factor, of the sixth degree, can only be solved approximately.

In order that this phenomenon in refraction may be observed experimentally, it is advisable to solve these equations for definite crystals. As a type of uniaxial crystal Iceland spar was chosen. The minimum value for  $\alpha$  (the surface is then tangent to the envelope) is found from the equation

$$\tan^2 \alpha = x^2/z^2 = x^2(1/a^2 + 1/b^2) + \frac{2x^3}{ab} \sqrt{\frac{1}{x^2 - b^2}}.$$

The indices of refraction for spar given by Mascart are  $1/a = 1.48654$  and  $1/b = 1.65846$  for the D line. The minimum value of  $\alpha = 69^\circ 32' 30''$ ; the corresponding coordinates of the point on the locus are  $x = \pm 0.695$  and  $z = \pm 0.2593$ .

The equation of a tangent to the circle from the above point is

$$x \cos \delta + z \sin \delta = b,$$

where  $\delta$  is the angle between the ray in the crystal and the optic axis X. Substituting the values for the remaining terms of the expression,  $\delta = 56^\circ 4'$ . The angle made by the normal to the surface and the ray, that is the angle of refraction, equals  $\phi = (90 - \alpha) + (90 - \delta) = 54^\circ 23' 30''$ . From those angles,  $\alpha$  and  $\phi$ , the minimum and maximum values for the refractive index of a medium that will permit this ray to pass through it, assuming the ray to pass the bounding medium from the crystal, may be found. For, let the angle

of the ray in the medium be  $90^\circ$ , and the angle in the crystal  $\phi$ ; then by the ordinary sine law the refractive index of the medium is 1.3484. On the other hand, if the angle in the medium be  $90^\circ$ , and the angle in the crystal be  $\alpha$ , as given above, then the refractive index of the medium is 1.5539. Or, in other words, if the refractive index of the medium is less than 1.3484, there can only be one ray which will enter the crystal, however it is cut, without divergence, and that is along the optic axis. If  $1.3484 < 1/d < 1.5539$ , there are two directions of non-divergence, and if  $1/d > 1.5539$ , three ; one always being in the direction of the optic axis.

Having established the necessary conditions for the bounding medium, it is possible to determine a section of Iceland spar which will give three coincident pairs of ordinary and extraordinary rays. The equation of the envelope (b) is put for calculation in the form

$$(\sin^2\theta - m_0^2 \sin^2\alpha) \{ A \sin^6\theta + B \sin^4\theta + C \sin^2\theta + D \} = 0,$$

where

$$A = -1/\cos^4\alpha,$$

$$B = \left\{ \frac{m_0^2 \sin^2\alpha}{\cos^4\alpha} + 2(m_0^2 + m_e^2) \frac{1}{\cos^2\alpha} \right\},$$

$$C = - \left\{ 2m_0^2(m_0^2 + m_e^2) \frac{\sin^2\alpha}{\cos^2\alpha} + (m_0^2 + m_e^2)^2 \right\},$$

$$D = m_0^2 \sin^2\alpha (m_0^2 - m_e^2)^2.$$

From the refractive indices of spar given above,  $m_0 = 1.65846/1.63034$  and  $m_e = 1.48654/1.63034$ .  $\alpha$  is taken equal to  $77^\circ$ . Substituting these values in the equation,

$$(\sin^2\theta - m_0^2 \sin^2\alpha) \{ 390.524 \sin^6\theta - 457.418 \sin^4\theta + 75.941 \sin^2\theta - 0.0308 \} = 0.$$

The roots by approximation are :— $\theta' = 80^\circ 13'$ ,  $\theta'' = 26^\circ 33'$ ,  $\theta''' = -82^\circ 23'$ . The last value gives the direction of a ray which will be refracted undivided along the optic axis. The fourth pair of roots is due to the intersection of the surface with the dotted branch of the locus, and is here, as afterwards, omitted.

If the surface is tangent to the locus, there are only two solutions. Here  $\alpha = 69^\circ 32' 30''$ ;  $\theta' = \theta'' = 55^\circ 47' 45''$ ; and  $\theta''' = -72^\circ 22' 50''$ .

*Solution for a Biaxal Crystal.*—The calculations are for aragonite, as it has an elliptic section of considerable eccentricity.

*1st Case.*—The ellipse and circle intersect (fig. 2). Upon substituting the values  $z=d\frac{\cos \alpha}{\sin \theta}$ ,  $x=-d\frac{\sin \alpha}{\sin \theta}$  in the equation (a) of the locus, we obtain

$$\begin{aligned} & \frac{\nu_3}{d^8 \sin^4 \alpha \cos^4 \alpha} \sin^8 \theta + \left( \frac{\nu_2}{d^6 \sin^2 \alpha \cos^4 \alpha} + \frac{2\mu_3}{d^6 \sin^4 \alpha \cos^2 \alpha} \right) \sin^6 \theta + \left( \frac{\nu_1}{d^4 \cos^4 \alpha} \right. \\ & \left. + \frac{2\mu_2}{d^4 \sin^2 \alpha \cos^2 \alpha} + \frac{\lambda_3}{d^4 \sin^4 \alpha} \right) \sin^4 \theta + \left( \frac{2\mu_1}{d^2 \cos^2 \alpha} + \frac{\lambda_2}{d^2 \sin^2 \alpha} \right) \sin^2 \theta + \lambda_1 = 0. \end{aligned}$$

Using carbon bisulphide as a bounding medium,  $1/d = 1.63034$ . For aragonite, Rudberg gives the following indices of refraction:— $1/a = 1.53013$ ,  $1/b = 1.68157$ ,  $1/c = 1.68589$ , for the D line.

Let the surface of the crystal intersect a conical point; from Rudberg's values  $\alpha = 81^\circ 4' 47''$ . Here it was possible to confirm the correctness of equation (a); as the coordinates of a conical point are readily found, they may be introduced into the equation of the locus which should then vanish. This was done, and the correctness of the equation verified. To return from this digression, the values of the constants were substituted, giving

$$\begin{aligned} & 1.45067 \sin^8 \theta - 3.23411 \sin^6 \theta + 1.93912 \sin^4 \theta \\ & - 0.15038 \sin^2 \theta + 0.0000321 = 0. \end{aligned}$$

Two roots are coincident, and the ray in the crystal grazes the surface; as  $1/b > 1/d$ , it cannot pass into the bounding medium, and the roots are imaginary. The other root is  $1^\circ 30' 15''$ .

Bounding medium again carbon bisulphide;  $\alpha = 86^\circ$ .

$$\begin{aligned} & 34.06891 \sin^8 \theta - 74.87614 \sin^6 \theta + 41.80691 \sin^4 \theta \\ & - 0.72988 \sin^2 \theta + 0.0000321 = 0. \end{aligned}$$

$\theta'' = 7^\circ 42' 30''$ . Other roots are imaginary.

As it was found to be very difficult to choose a value for  $\alpha$  that would give three real roots, a somewhat more indirect method was adopted. If we assume a medium with a refractive index exactly equal to that of the circular section of the crystal, then the coincident rays will not deviate in

passing from one to the other; so if the surface cuts the locus in three points each must give a real solution. Let the refractive index of this medium be  $1/d' = 1/b$  and let  $\alpha = 75^\circ$ , then

$$0.26194 \sin^8 \theta_1 - 0.56635 \sin^6 \theta_1 + 0.36460 \sin^4 \theta_1 \\ - 0.05986 \sin^2 \theta_1 + 0.0000321 = 0.$$

The roots are  $\theta'_1 = 76^\circ 40'$ ,  $\theta''_1 = 29^\circ 56' 30''$ ,  $\theta'''_1 = -79^\circ 15'$ . The fluids which most nearly agree with this condition are those of the bromo-naphthaline group. Since the above rays are not deviated, we may consider them to be the rays in the crystal and find the corresponding rays in the medium, substituting naphthaline, by the sine law, as they obey the ordinary law of refraction.

Medium, —  $\alpha$  mono-bromo-naphthaline. Walter gives  $1/d = 1.65820$  at  $20^\circ$ . As  $1/b = 1.68157$ ,  $\theta' = 80^\circ 39' 57''$ ,  $\theta'' = 30^\circ 24' 30''$ ,  $\theta''' = -85^\circ 4' 3''$ .

Medium, —  $\beta$  mono-bromo-naphthaline.  $1/d = 1.66138$  (Gladstone);  $\theta' = 79^\circ 33' 28''$ ,  $\theta'' = 30^\circ 17' 40''$ ,  $\theta''' = -83^\circ 11' 20''$ .

*2nd Case.*—Circle within ellipse (fig. 3). The equation of the locus is the same as in the first case except that the symbols  $b$  and  $c$ ,  $y$  and  $z$  are interchanged.

With a bounding medium of carbon bisulphide and  $\alpha = 77^\circ$ ,

$$0.32965 \sin^8 \theta - 0.71619 \sin^6 \theta + 0.45578 \sin^4 \theta \\ - 0.06980 \sin^2 \theta + 0.000029 = 0.$$

The roots are,  $\theta' = 73^\circ 48'$ ,  $\theta'' = 28^\circ 10'$ ;  $\theta'''$  is imaginary.

*3rd Case.*—Ellipse within circle (fig. 4). No calculations were made for this section, as even for aragonite, which has a relatively large difference between the three refractive indices, the elliptic wave-front is practically a circle. So that there is little that is characteristic for this section.

The asymptotes of the envelope, when the crystal is spar, are

$$z = \pm \frac{ab}{a+b} = \pm 0.31797.$$

The real points on the axes are

$$x = \pm b = \pm 0.60297; z = \pm \frac{ab}{(a^2+b^2)^{\frac{1}{2}}} = \pm 0.44901.$$

The asymptotes for aragonite are, as given earlier in the paper,

$$\lambda_1 x^4 + \lambda_2 x^2 + \lambda_3 = 0, \\ \lambda_1 z^4 + 2\mu_1 z^2 + \nu_1 = 0.$$

When ellipse and circle intersect,

$$x = \pm 0.58601, \quad z = \pm 0.31945.$$

When ellipse is outside circle,

$$x = \pm 0.60202, \quad y = \pm 0.30250.$$

The real intersections on the axes are

$$\nu_1 x^4 + \nu_2 x^2 + \nu_3 = 0,$$

$$\lambda_3 z^4 + 2\mu_3 z^2 + \nu_3 = 0.$$

When ellipse and circle intersect,

$$x = \pm 0.58619, \quad z = 0.44278.$$

When ellipse is outside circle,

$$x = \pm 0.60257, \quad y = 0.43628.$$

As the difference in lengths of axes of the crystals has been much exaggerated in the diagrams, only the relative positions of these points and lines are shown.

A word should be said regarding the physical interpretation of the parts of the locus hitherto omitted. A supposititious case of refraction, which cannot be realized, may be given to explain the existence of the dotted branches of the curve. If a source of light were situated at the origin of coordinates, emitting an ordinary and extraordinary ray in opposite directions, then the locus which would give coincidence of direction to these rays is the dotted curves indicated.

I have not been able to interpret the presence of the singular points on the axes. When the intersections on the axes are singular points they always lie *inside* both the ellipse and the circle. The two tangents to the ellipse and circle, which are the wave-fronts of the rays of light, are consequently imaginary. It seems, then, as if the rays also must be imaginary.

**XXII. Viscosity of Solutions.** *By R. Hosking, Kernal Research Scholar in the University of Melbourne\*.*

**I**T is evident that, in the immediate future, the study of the viscosity of liquids is destined to prove as helpful in the investigation of the molecular kinetics of liquids as the corresponding study of gaseous viscosity has been found to be in the kinetic theory of gases.

Already a large amount of work on the viscosity of liquids has been published, but much of the pioneer work has been

\* Communicated by Mr. W. Sutherland on behalf of Prof.

superseded by the recent careful measurements of Thorpe and Rodger (*Phil. Trans.* 1894).

The object of the present experimental investigation is to bring the data for some typical solutions up to at least the standard of completeness attained by Thorpe and Rodger for the commoner liquids ; for it is probable that in the next important advance in the theory of solutions, viscosity will have a considerable share. The solutions chosen for study were those of NaCl 1 per cent., 5 per cent., 10 per cent., and 20 per cent., representing typical electrolytic solutions ; and of cane-sugar 1 per cent., 5 per cent., 10 per cent., 20 per cent., and 40 per cent., representing typical non-electrolytic solutions. Absolute values of the viscosity were obtained over a range of temperature from 0° to 90° C.

To ascertain whether the viscosities of these solutions had been determined to the desired degree of accuracy, a preliminary study of the viscosity of water over the same range of temperature was undertaken ; and as it was found that the results were in accord with the best determinations hitherto made, such as those of Poiseuille, Sprung, Slotte, and Thorpe and Rodger, it was concluded that the viscosities of solutions obtained with the same apparatus could be taken to possess the desired degree of accuracy.

In the tables containing the data obtained in these experiments, those for water will be given along with the values for solutions.

The method employed was that used by Thorpe and Rodger, the general principles of which are here stated.

A definite volume of the liquid under observation, under the influence of a definite pressure, flows through a horizontal capillary tube of known dimensions in a certain time, the temperature of the liquid being observed and kept constant during the interval.

The liquid, for the purposes of experiment, was contained in a glass glischrometer, similar to that employed by Thorpe and Rodger, with the difference, however, that the short capillary tube, instead of being sealed to the two limbs, was united to them by means of two indiarubber corks, one at each end of the capillary tube.

The glischrometer was almost completely immersed in a water-bath, which was heated to the desired temperature by gas-flames, and could be maintained at that temperature by manipulation of a very small jet applied beneath it.

On each vertical limb of the glischrometer two horizontal marks were etched, in the restricted portions above and below the long cylindrical bulbs ; the two limbs had been made

perfectly similar in size and shape, and so the two marks on either limb were placed symmetrically with regard to the bulb between them, and, when the capillary tube was horizontal, and limbs vertical, the two upper marks were in the same horizontal plane, and likewise the two lower ones.

The volume of liquid employed in the experiments is that which the glischrometer holds when the one meniscus is level with the upper mark in the one limb, and the other meniscus coincides with the lower mark in the other limb. The volume which flows through the capillary, however, is that contained between the two marks on the same limb, diminished by the small quantity which adheres to the sides of the bulb.

The pressure is that due to a reservoir of compressed air, which can be connected to either limb at pleasure, and is measured by an open water-manometer.

The time of flow is measured by a stop-watch, and the temperature of the liquid is that of the bath surrounding it, and is indicated by thermometers graduated to tenths.

#### *Measurement of the Constants of the Glischrometer.*

These constants are the semi-axes of the capillary, the working length of the capillary, and the working volume of the bulbs, where the working length of the capillary means the measured length together with the Couette correction for the open ends, and the working volume means the quantity of liquid which flows through the capillary in an experiment. These constants are determined before the portions of the glischrometer are united together.

The capillary tube was selected and cut from a much longer piece which had been previously calibrated with extreme care, and of which the mean diameter had been obtained by weighing the mercury which had occupied known lengths in the tube. The mean diameter of the selected portion was deduced. The bore was slightly elliptical, and the ratio of the axes was observed directly under a microscope. From these two series of measurements, the values of the semi-axes were obtained. The length of the capillary was measured directly, the ends having been previously ground perpendicular to the length of the bore.

To obtain the working volume of the bulbs, a suitable capillary tube was attached to the lower extremity of the limb, and the limb filled with water. The pressure was then applied above, and the liquid was driven through at about the same rate as it would be in the ordinary experiments. The discharge from the instant when the meniscus passed the upper

mark to that when it crossed the lower mark was caught in a weighed flask and immediately weighed.

The only disadvantage of the use of corks instead of making the whole glischrometer of glass and sealing the capillary and limbs together, is that a ring of rubber 8 millim. in mean diameter and 0·5 millim. in width is in contact with the liquid at each end of the capillary tube ; but in the case of aqueous solutions there is nothing to fear in the way of dissolved rubber. By the use of corks, on the other hand, in addition to the fact that the constants of the glischrometer can be evaluated before uniting the limbs and capillary, we have the further advantages that cleaning operations are much facilitated, risk of breakage is diminished, and capillary tubes of different dimensions can readily be substituted if necessary.

The following values were obtained for the constants :—

Semi-major-axis of capillary (A)	= 0·012165 cm.
Semi-minor axis of capillary (B)	= 0·011525 "
Mean diameter of capillary (D)	= 0·023681 "
Length of capillary . . . (L)	= 5·3570 "
Couette correction to length (l)	= 0·0190 "
Working length of capillary (L+l)	= 5·3760 "
Volume of right limb , . . (V <sub>R</sub> )	= 5·240 c. cm.
Volume of left limb . . . (V <sub>L</sub> )	= 5·241 "

The formula from which the values of the viscosity are found is

$$\eta = \frac{\pi A^3 B^3 G \rho h T}{4V(A^2 + B^2)(L + l)} - \frac{ABV}{4\pi(A^2 + B^2)(L + l)} \frac{\delta}{T} (1 + 2\beta t);$$

where the second term represents the kinetic-energy correction, and

$\eta$  is the viscosity coefficient,

G is the value of the acceleration due to gravity,

$\rho$  is the density of water in the water-manometer,

$h$  is the height of water in the manometer,

T is the time taken for volume V to flow through the capillary under pressure G  $\rho$  h,

$\delta$  is the density of liquid under observation at the particular temperature ; and

(1+2 $\beta$ t) is the correcting term for expansion of the glass, where  $\beta$  is the linear coefficient of expansion, and t is the temperature of the experiment.

The formula then becomes

$$\eta = \alpha \times \rho \times h \times T - \beta \times \frac{\delta}{T} \times (1 + 2\beta t),$$

and

$$\log \alpha = 7.4282145; \quad \log \beta = 2.5880686.$$

All the necessary corrections were made to the readings of the stop-watch, the thermometers, and the pressure-gauge. The flow through the capillary tube was in every case linear, and the kinetic-energy correction comparatively small.

Care was taken that the liquid should remain free from dust throughout the whole series of observations. The amount of liquid in the glischrometer was so regulated that at each temperature the volume should be unaltered. The observations were begun at low temperatures in every case; and when the liquid in the glischrometer had reached the next higher temperature, the increase in volume was extracted.

The air-reservoir was a large copper cylinder connected with a pump on the one side, and on the other side with the manometer and two glass three-way taps, by means of rubber tubing and T-pieces. The two taps were united by rubber tubing to the limbs of the glischrometer, one to each, and the liquid in the glischrometer could be driven in either direction by proper adjustment of the taps.

The bath was provided with the necessary taps and syphons for filling and emptying it, and, in addition, for running a continuous stream of cold water through the bath for temperatures below the normal.

The glischrometer, thermometer, and siphon-tubes were kept in position by the cover of the bath, through which suitable holes had been bored. Another hole in the cover admitted the shaft of a small propeller for stirring the water of the bath, with power taken from a small water-motor. When the propeller was rotated quickly by this means, a splendid circulation was set up in the bath.

In explanation of the accompanying tables, the following short description of the order of observations may be necessary.

Imagine that the observations are complete at one temperature, and the bath is being heated to the next temperature at which we desire to make a measurement.

When this temperature has been reached, the stirrer is set in motion and the regulating flame increased to prevent cooling: when the temperature remains practically constant, the liquid is driven into the right limb by turning the left tap to pressure and the right to air: when the meniscus in the left limb has reached the lower mark, the left tap is also turned to air, and the indiarubber from the top of the

right limb having been just previously removed, the extra quantity of liquid due to expansion is withdrawn by a suitable instrument, the meniscus being made to coincide with the upper mark on the right limb when the meniscus in the left limb coincides with the lower mark on that side. Connexion is again restored between the right limb and the right tap.

The left tap is now for a few seconds turned to pressure, and then the right tap is turned also.

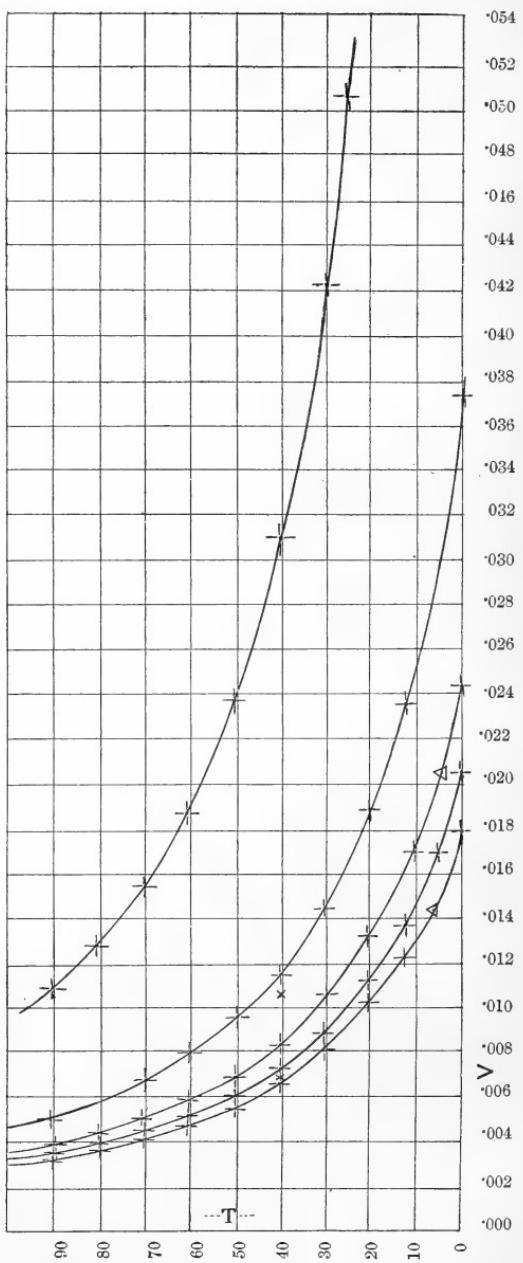
The first reading of the pressure is now taken, and the left tap turned to air. The upper mark in R (=right side) is observed through a telescope, and, when the meniscus crosses it, the watch is started. Immediately the first reading of the temperature is made, through another telescope. The first telescope is moved down on its graduated vertical scale to view the lower mark in R.

The stop-watch is stopped at the instant of coincidence, the second reading of the temperature is taken, and the left tap turned to pressure. The second reading of the pressure is now taken. A second set of observations is taken with the liquid flowing in the opposite direction. When this set is complete, the stirrer is stopped, unless the whole set is to be repeated, and the experiment at this particular temperature is at an end.

The value for the viscosity is determined for each set of readings; and if the temperature has remained unaltered, the mean of the two values is taken as the first absolute value at that temperature. A second absolute value is obtained from the third and fourth sets of observations, that is the second complete set: here a complete set represents two ordinary sets—one from right to left, and the other from left to right.

The temperature, however, usually alters slightly during an experiment at a particular temperature; and we may obtain four different readings of the mean temperature and four different values of the viscosity. We have then to reduce these four values to what they would be at the mean of the four temperatures, for which purpose the value of  $d\eta/dt$  is obtained from a curve drawn through the points representing the first values of viscosity and temperature in each set, and by means of it the four values are reduced to values at the mean temperature. Then, as before, the mean of the first and second values gives the first mean value, and the mean of the third and fourth the second mean value. The mean of these values is taken as the final mean value.

Fig. 1.— Viscosity-Temperature Curves.  $C_{12}H_{22}O_{11}$  Solutions.

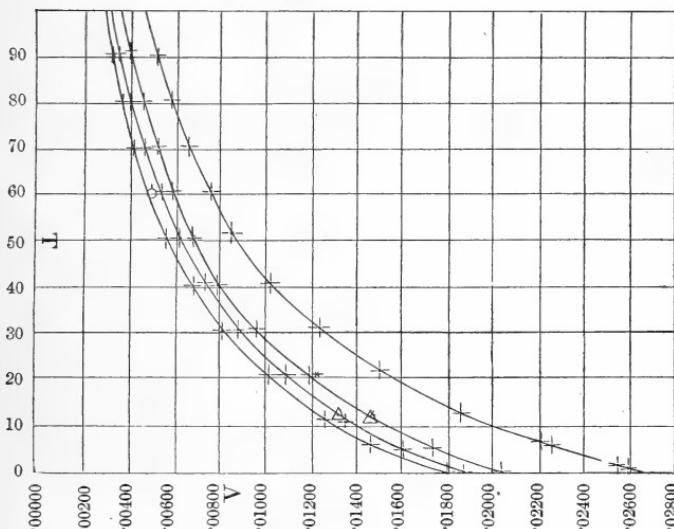


In Table I. will be found typical sets of observations and results calculated in the case of water at certain temperatures.

The mean pressure only has been given, but the difference between the first and second readings is always slight.

The value of the kinetic-energy correction is also shown in this table, and in the case of water at 90° it has its greatest relative value.

Fig. 2.—Viscosity-Temperature Curves. NaCl Solutions.



In Table II. the temperature is the mean, and the four values (1), (2), (3), (4) are the reduced values obtained as above.

In Table III. we have the interpolated results for water compared with those determined by other experimenters, whose values are those given by Thorpe and Rodger.

In Table IV. we have produced the final mean values only, except in the case of the 20-per-cent. solution, where in addition we have shown the first and second mean values.

The NaCl solutions were made from a sample of Schuchardt's "very pure" kindly supplied by Mr. W. P. Wilkinson, analyst, Melbourne.

The densities of these solutions are here given at 15° C.:—

	20 p. c.	10 p. c.	5 p. c.	1 p. c.
Observed .....	1.1494	1.0724	1.0355	1.0065
Bender's values (Wied. Ann. xxii.)	1.1497	1.0724	1.0355	—

TABLE I.—*Results.*

The following are typical examples of the observations for water at temperatures near  $0^{\circ}$ ,  $50^{\circ}$ ,  $90^{\circ}$ :

Direction of Flow.	Mean pressure tens. of water (corrected).	Temp. of Gauge.	Density.	Time (corrected).	Correction for kinetic energy (calculated).	Temperature (observed).	Mean Temperature.	Viscosity (calculated).
R. to L.	166.29	16	0.9999	6 43.4	-0.0096	{ 0.18 { 0.18 }	0.18	.01787
L. to R.	164.49	"	"	6 46.4	95	{ 0.18 { 0.18 }	0.18	.01781
R. to L.	162.54	"	"	6 52.0	94	{ 0.18 { 0.20 }	0.19	.01784
L. to R.	160.60	"	"	6 54.2	93	{ 0.28 { 0.34 }	0.31	.01772
R. to L.	99.33	15	0.9873	3 28.8	-0.00183	{ 51.85 { 51.85 }	51.85	.00537
L. to R.	98.83	"	"	3 29.0	183	{ 51.83 { 51.83 }	51.83	.00535
R. to L.	98.33	"	"	3 30.8	181	{ 51.82 { 51.82 }	51.82	.00537
L. to R.	97.83	"	"	3 31.0	181	{ 51.79 { 51.79 }	51.79	.00535
R. to L.	87.79	16	0.9655	2 27.0	-0.00254	{ 90.10 { 90.06 }	90.08	.00320
L. to R.	87.64	"	"	2 27.4	254	{ 90.00 { 90.00 }	90.00	.00320
R. to L.	87.54	"	"	2 28.0	253	{ 90.00 { 90.00 }	90.00	.00322
L. to R.	87.49	"	"	2 28.0	253	{ 90.00 { 90.02 }	90.01	.00321

In Table V. we have the interpolated results for NaCl.

In Table VI. the final mean values only, for sugar solutions. The sample of sugar used was supplied by Professor Masson. The densities of the solutions at 17°·5 C. are here given:—

	40 p. c.	20 p. c.	10 p. c.	5 p. c.	1 p. c.
Observed . . . . .	1·1790	1·0830	1·0403	1·0192	1·0033
Watt's Dict. of Chem. (last ed.)	1·1794	1·0833	1·0401	1·0197	—

And in Table VII. the interpolated values for sugar solutions are reproduced.

For the purposes of interpolation the results were plotted on a suitably large scale. The results are herewith shown plotted on a smaller scale in figs. 1 & 2 (pp. 280, 281). A value of the viscosity at ordinary temperatures was sometimes obtained after the liquid had been heated above 90°, cooled down again, and allowed to remain, in some cases 24 and in others 36 hours, in the glischrometer. These observations are indicated in a different way in the accompanying curves, to the ordinary observations.

TABLE II.—Water.

Temp.	Viscosities.				
	(1) R. to L.	(2) L. to R.	(3) R. to L.	(4) L. to R.	Mean.
0°21	.01785	.01778	.01783	.01778	.01781
2°37	.01655	.01653	.01658	.01656	.01656
6°53	.01456	.01451	.01455	.01450	.01453
9°89	.01316	.01314	.013145	.01314	.01315
12°44	.01227	.01222	.01222	.01220	.01223
20°72	.00992	.00990	.00991	.00990	.00991
30°78	.007895	.00788	.007885	.00788	.007885
41°74	.006385	.006385	.00637	.00638	.00638
51°82	.00537	.00535	.00537	.00534	.00536
60°67	.00467	.00466	.00468	.00467	.00467
71°58	{ .00400 .00401	{ .00399 .00398	{ .00399 .00399	{ .00398 .00398 }	{ .00399 .00399 }
81°19	{ .00355 .00355	{ .00354 .00354	{ .00356 .00355	{ .00353 .00354 }	{ .003545 .003545 }
90°10	{ .003195 .00321	{ .00319 .00321 }	.00320	.00320	.00320

TABLE III.—Interpolated Results (Water).

Temp.	1846. Poiseuille.	1876. Sprung.	1883. Slotte.	1894. Thorpe & Rodger.	1899.
0°	.01776	.01778	.01808	.01778	.01794
5	.01515	.01510	.01524	.01510	.01520
10	.01309	.01301	.01314	.01303	.01309
15	.01146	.01135	.01144	.01134	.01143
20	.01008	.01003	.01008	.01002	.01009
25	.00897	.00896	.00898	.00891	.00897
30	.00803	.00802	.00803	.00798	.00802
35	.00721	.00723	.00724	.00720	.00724
40	.00653	.00657	.00657	.00654	.00657
45	.00595	.00602	.00602	.00597	.00601
50	.....	.00553	.00553	.00548	.00553
55	.....	.....	.00510	.00506	.00510
60	.....	.....	.00472	.00468	.00472
65	.....	.....	.00438	.00436	.00437
70	.....	....	.00408	.00406	.00407
75	.....	.....	.00382	.00380	.00382
80	.....	.....	.00358	.00356	.00360
85	.....	.....	.00337	.00335	.00339
90	.....	.....	.00318	.00316	.00320
95	.....	.....	.00301	.00299	
100	.....	.....	.00285	.00283	

TABLE IV.—NaCl Solutions.

Temp.	20 per cent.			10 per cent.			5 per cent.			1 per cent.		
	(1) Viscosity.	(2) Viscosity.	Mean Viscosity.	Temp.	Viscosity.	Temp.	Viscosity.	Temp.	Viscosity.	Temp.	Viscosity.	
0°22	.02591	.....	.02591	0°06	.02035	0°00	.01861	0°00	.01798			
1°24	.02547	.....	.02547									
5°46	.02240	.....	.02240	4°99	.01738	4°90	.01605	6°39	.01460			
5°95	.02203	.....	.02203									
12°48	.018465	.01848	.01847	11°80	.01450	10°89	.01357	11°76	.01254			
21°20	.01499	.01498	.01499	20°46	.01181	20°22	.01078	20°26	.01009			
30°69	.01221	.01222	.01222	30°72	.00947	30°12	.00872	30°08	.00809			
40°57	.01014	.01013	.01013	40°30	.00797	40°86	.00714	40°15	.00664			
51°65	.00842	.00843	.008425	50°72	.00671	50°19	.00614	50°42	.00565			
60°65	.00736	.00737	.00736	60°67	.00584	60°84	.00524	60°39	.00486			
70°62	.006415	.00642	.00642	70°72	.00512	70°10	.00455	70°10	.00416			
80°88	.00566	.00565	.00565	80°27	.00452	80°25	.00398	80°32	.00366			
90°60	.00504	.00504	.00504	91°30	.00396	90°60	.003515	90°24	.00324			

TABLE V.—Interpolated Results (NaCl).

Temp.	Viscosities.			
	1 per cent.	5 per cent.	10 per cent.	20 per cent.
0 .....	.01799	.01862	.02041	.02666
5 .....	.01534	.01600	.01738	.02269
10 .....	.01320	.01390	.01528	.01968
15 .....	.01154	.01223	.01345	.01733
20 .....	.01018	.01083	.01194	.01540
25 .....	.00905	.00973	.01066	.01378
30 .....	.00810	.00876	.00961	.01239
35 .....	.00731	.00796	.00875	.01124
40 .....	.00666	.00725	.00802	.01025
45 .....	.00609	.00666	.00737	.00939
50 .....	.00559	.00614	.00680	.00866
55 .....	.00519	.00569	.00633	.00801
60 .....	.00481	.00531	.00589	.00744
65 .....	.00448	.00492	.00550	.00693
70 .....	.00416	.00456	.00516	.00649
75 .....	.00391	.00425	.00484	.00607
80 .....	.00368	.00399	.00455	.00571
85 .....	.00346	.00375	.00427	.00537
90 .....	.00325	.00355	.00401	.00507

TABLE VI.—Sugar Solutions.

40 per cent.		20 per cent.		10 per cent.		5 per cent.		1 per cent.	
Temp.	Viscosity	Temp.	Viscosity	Temp.	Viscosity	Temp.	Viscosity	Temp.	Viscosity
0°00	.1476	0°00	.03720	0°00	.02436	0°10	.02038	0°10	.01801
8°87	.0939	5°43	.03002	5°10	.02042	5°26	.01716	7°10	.01437
12°79	.0798	13°02	.02351	10°42	.01722	12°58	.01381	13°32	.01218
20°23	.06004	20°04	.01910	20°17	.01322	20°29	.01127	20°00	.01031
29°98	.04233	30°44	.01466	29°89	.01044	30°43	.00889	30°43	.00804
40°44	.03100	40°31	.01171	40°30	.00838	40°40	.00725	40°18	.00667
50°31	.02390	50°30	.00952	50°35	.00696	50°46	.00605	50°13	.00554
60°51	.01884	60°20	.00797	60°27	.00590	60°34	.00517	60°54	.00470
70°06	.01550	70°06	.00675	70°36	.00509	70°25	.00449	70°04	.00410
80°32	.01279	80°21	.00583	80°31	.00446	80°00	.00399	80°06	.003615
90°11	.01086	90°21	.00509	89°78	.00390	89°84	.003505	90°00	.00320

TABLE VII.—Interpolated Results ( $C_{12}H_{22}O_{11}$ ).

Temp.	Viscosities.				
	1 per cent.	5 per cent.	10 per cent.	20 per cent.	40 per cent.
0 .....	.01810	.02048	.02436	.03720	.1476
5 .....	.01537	.01729	.02050	.03042	.1133
10 .....	.01331	.01488	.01754	.02578	.0895
15 .....	.01168	.01292	.01518	.02212	.0730
20 .....	.01031	.01139	.01328	.01910	.0607
25 .....	.00911	.01009	.01173	.01674	.0508
30 .....	.00812	.00901	.01041	.01485	.04233
35 .....	.00737	.00809	.00933	.01319	.03618
40 .....	.00670	.00732	.00843	.01180	.03132
45 .....	.00609	.00668	.00763	.01059	.02728
50 .....	.00555	.00611	.00699	.00961	.02410
55 .....	.00511	.00564	.00640	.00872	.02140
60 .....	.00473	.00521	.00592	.00799	.01908
65 .....	.00438	.00487	.00549	.00732	.01722
70 .....	.00410	.00455	.00512	.00676	.01553
75 .....	.00387	.00427	.00480	.00629	.01414
80 .....	.00362	.00399	.00448	.00586	.01288
85 .....	.00340	.00377	.00421	.00548	.01182
90 .....	.00320	.00349	.00389	.00511	.01093

My best thanks for valuable advice and direction are due to T. R. Lyle, M.A., Professor of Natural Philosophy, E. F. J. Love, M.A., F.R.A.S., Demonstrator and Assistant Lecturer in Natural Philosophy, D. Orme Masson, M.A., D.Sc., F.R.S.E., Professor of Chemistry, and to J. M. Baldwin, B.A., who plotted the curves with a considerable amount of care and painstaking.

Physical Laboratory,  
Melbourne University,  
Dec. 11, 1899.

### XXIII. On the Thermal Conductivities of Mixtures and of their Constituents. By CHARLES H. LEES, D.Sc.\*

THOSE physicists who have endeavoured to express the thermal conductivities of physical mixtures in terms of the conductivities of their constituents, and the amount of each present, have made use of the formulæ

\* Communicated by the Physical Society: read November 24, 1899.

$$k = \frac{p_1 k_1 + p_2 k_2}{p_1 + p_2}, \dots \quad (1)$$

$$\frac{1}{k} = \frac{p_1 \frac{1}{k_1} + p_2 \frac{1}{k_2}}{p_1 + p_2}, \dots \quad (2)$$

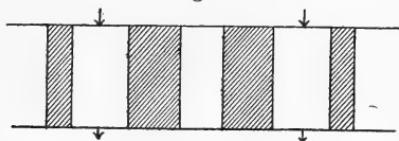
where  $k_1$  and  $k_2$  are the conductivities of the constituents, and  $p_1$  and  $p_2$  either the masses or the volumes of each present. Paalhorn, Winkelmann, and Schott, in their paper on the conductivities of glasses \*, used the first form with the  $p$ 's the masses of the constituents present; but Winkelmann has recently recalculated the results †, using the second form, with the  $p$ 's the volumes of the constituents present, and found a better agreement than formerly.

Focke ‡ uses the first formula, with the  $p$ 's the masses, to represent his own results on the conductivities of various kinds of glass. Both theory and experiment §, however, point to the fact that it is the proportion by volume which ought to be used in such calculations; and I shall confine myself in what follows to the consideration of the proportions by volume, calculated on the assumption that the mixture is simply a physical mixture, and is formed without contraction. Under these conditions the formula

$$k = \frac{p_1 k_1 + p_2 k_2}{p_1 + p_2}$$

corresponds to the constituents being distributed in the space between the two parallel isothermal surfaces, through which the heat enters and leaves the medium, in the form of right prisms with their axes perpendicular to these surfaces, thus:—

Fig. 1.



and the formula

$$\frac{1}{k} = \frac{p_1 \frac{1}{k_1} + p_2 \frac{1}{k_2}}{p_1 + p_2}$$

\* Wied. *Ann.* li. p. 738 (1894)

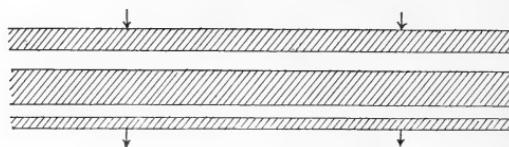
† *Ibid.* lxvii. p. 160 (1899).

‡ *Ibid.* lxvii. p. 155 (1899).

§ Lees, *Phil. Trans. Royal Society*, exci. p. 433 (1898); *Phil. Mag. ante*, p. 224.

to their being distributed in layers parallel to the isothermal surfaces, thus :—

Fig. 2.

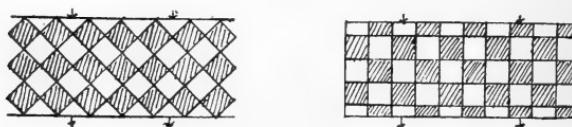


It has been recently shown \* that the formula

$$\log k = \frac{p_1 \log k_1 + p_2 \log k_2}{p_1 + p_2} \dots \dots \quad (3)$$

corresponds to a prismatic distribution which, in the case of equal volumes of the constituents being present, is represented in section thus :—

Fig. 3.



As it is not easy to say that one of these three distributions is more likely than another to represent the actual facts, I propose to apply each of the three formulæ to the calculation of the conductivities of the mixtures of solids and liquids experimented on by G. Wiedemann †, Henneberg ‡, and myself §, and compare the results of the calculations with the values found experimentally.

It will be noticed that the conductivities determined for successive equal increments of one constituent, correspond for the first formula to the successive terms of an arithmetic, for the second to the terms of a harmonic, and for the third to those of a geometric series, the first and the last terms of the three series being the same. The third formula will therefore give a value for the conductivity of a given mixture between the values given by the first and second formulæ. In the tables which follow the values calculated by the three formulæ (1), (2), and (3) are referred to as "mean conductivity," "mean resistivity," and "mean logarithmic" respectively.

\* Lees, Phil. Mag. *ante*, p. 226 (1900).

† G. Wiedemann, Pogg. Ann. cviii. p. 393 (1859).

‡ Henneberg, Wied. Ann. xxxvi. p. 146 (1889).

§ Lees, Phil. Trans. Royal Soc. cxvi. p. 399 (1898).

## Tin-Bismuth Alloy \* (Wiedemann).

Composition by volume.	$k$ observed, Ag = 100.	$k$ calculated.					
		Mean cond.	Error p. c.	Mean resist.	Error p. c.	Mean log.	Error p. c.
Sn .....	15.2						
,, 20 p. c. Bi .....	10.1	12.5	+ 24	6.1	- 40	9.9	- 2
,, 42.7 p. c. Bi .....	5.6	9.5	+ 70	3.6	- 36	6.1	+ 11
,, 69.1 p. c. Bi.....	2.3	5.9	+ 156	2.5	+ 8.7	3.5	+ 52
Bi .....	1.8						

## Dilute Ethyl Alcohol (Henneberg).

Composition by volume.	$k$ obs.	$k$ calculated.					
		Mean cond.	Error p. cent.	Mean resist.	Error p. cent.	Mean log.	Error p. cent.
Water .....	100						
,, 12.4 p. c. Ethyl Ale....	91	91.3	+ 3	78.0	- 14	86.1	- 5.4
,, 24.5 " " .....	81.4	82.9	+ 2	63.8	- 22	74.5	- 8.5
,, 36.1 " " .....	73.1	74.8	+ 2	54.4	- 26	64.9	- 11
,, 47.3 " " .....	64.6	66.9	+ 4	47.7	- 26	56.8	- 12
,, 57.8 " " .....	54.6	59.6	+ 9	42.7	- 22	50.0	- 8
,, 67.7 " " .....	47.6	52.7	+ 11	38.9	- 18	44.4	- 7
,, 76.9 " " .....	41.7	46.3	+ 11	35.9	- 14	39.7	- 5
,, 85.4 " " .....	37.5	40.3	+ 7	33.5	- 11	35.9	- 4
,, 93.2 " " .....	32.1	34.9	+ 9	31.6	- 2	32.7	- 2
Ethyl Alcohol .....	30.1						

## Water and Glycerine.

Water .....	0.0140						
,, 20.8 p. c. Glycerine ..	119	125	+ 5	116	- 3	121	+ 2
,, 44.2 " " .....	101	109	+ 8	97	- 4	103	+ 2
,, 70.4 " " .....	81	91	+ 12	82	- 1	86	+ 6
Glycerine .....	70						

## Water and Ethyl Alcohol.

Water .....	0.0149						
,, 30 p. c. Alcohol .....	104	118	+ 13	99	- 5	105	+ 1
,, 58 " " .....	79	90	+ 14	66	- 16	76.4	- 3
,, 81 " " .....	59	60	+ 12	54	- 8	58.5	- 1
Ethyl Alcohol .....	47						

\* Wiedemann's copper-zinc results appear to exclude this alloy from the class of physical mixtures.

Composition by volume.	<i>k</i> obs.	<i>k</i> calculated.					
		Mean cond.	Error p. cent.	Mean resist.	Error p. cent.	Mean log.	Error p. cent.
Water .....	00149						
" 24 p. c. Acetic Acid .....	118	124	+ 5	94	-20	110	-7
" 48·7 " .....	88	97	+10	68	-23	82	-7
" 74 " .....	64	71	+11	53	-17	59	-8
Acetic Acid .....	43						

## Water and Methyl Alcohol.

Water .....	00148						
" 28·8 p. c. Meth. Ale... .....	111	120	+ 8	97	-13	109	-2
" 58·0 " .....	80	92	+15	71	-11	81	-1
" 80·7 " .....	63	70	+11	59	- 6	64	-1
Methyl Alcohol .....	52						

## Ethyl Alcohol and Glycerine.

Ethyl Alcohol .....	00044						
"   " 17·4 p. c. Glyc. .....	43	49	+14	47	+9	48	+12
"   " 38·7 " .....	50	54	+ 8	51	+2	53	+ 4
"   " 65·3 " .....	56	61	+ 9	58	+4	60	+ 7
Glycerine .....	70						

## Methyl Alcohol and Ethyl Alcohol.

Methyl Alcohol .....	00052						
"   " 25 p. c. { Ethyl "   " Ale. } .....	50	505	+1	505	+1	505	+1
"   " 50 " .....	47	49	+4	49	+4	49	+4
"   " 75 " .....	46	475	+3	47	+2	475	+3
Ethyl Alcohol .....	46						

## Vaseline and Marble.

Vaseline .....	00044						
" 25 p. c. Marble .....	63	210	+233	57	-10	88	+40
" 43 " .....	108	330	+206	74	-31	145	+34
" 60 " .....	179	444	+149	102	-43	234	+31
Marble .....	710						

## Lard and Zinc Sulphate.

Lard .....	00047						
" 23·8 p. c. ZnSO <sub>4</sub> .....	59	60	+ 2	56	- 5	61	+3
" 37·5 " .....	74	84	+14	63	-15	72	+3
" 55·5 " .....	84	101	+20	75	-11	88	+5
Zinc Sulphate .....	145						

Without endeavouring to express the relative values of the three formulæ numerically, we may arrange the three in order of merit for each mixture as follows :—

	Order of merit of calculated Values.		
	Best.	Middle.	Worst.
Water and Ethyl Alcohol (Henneberg) .....	{ Conductivity. Logarithm. }	.....	Resistivity.
Water and Ethyl Alcohol (Lees) .....	Logarithm.	Resistivity.	Conductivity.
Water and Glycerine .....	Resistivity.	Logarithm.	Conductivity.
Water and Acetic Acid .....	Logarithm.	Conductivity.	Resistivity.
Water and Methyl Alcohol .....	Logarithm.	Resistivity.	Conductivity.
Ethyl Alcohol and Glycerine.....	Resistivity.	Logarithm.	Conductivity.
Ethyl Alcohol and Methyl Alcohol .....	{ Resistivity.		{ Conductivity. Logarithm.
Tin and Bismuth (Wiedemann) .....	Logarithm.	Resistivity.	Conductivity.
Vaseline and Marble .....	Resistivity.	Logarithm.	Conductivity.
Lard and Zinc Sulphate ...	Logarithm.	Resistivity.	Conductivity.

From this it will be seen that the formula

$$k = \frac{p_1 k_1 + p_2 k_2}{p_1 + p_2}$$

represents the observed results worst, and that of the other two the formula

$$\log k = \frac{p_1 \log k_1 + p_2 \log k_2}{p_1 + p_2}$$

is somewhat better than

$$\frac{1}{k} = \frac{\frac{1}{p_1 k_1} + \frac{1}{p_2 k_2}}{p_1 + p_2}.$$

The representation of the observed facts which even the best of the three gives is, however, only rough. As a rule the mean resistivity formula gives too low, and the mean logarithmic formula too high, values for the conductivity of each mixture. Now the conductivity of a compound built up of two materials, as in fig. 3, but with the same structure

also in a plane perpendicular to that of the drawing, *i. e.* consisting of cubes of the two media, will be greater than that of the prisms of fig. 3, and will therefore deviate more from the value of the conductivity found experimentally than does that given by the logarithmic formula. Hence it seems unnecessary to attempt an accurate calculation of the conductivity of the mixture of cubes. Also, since the deviations from the calculated values found in the cases considered in the above tables, appear to differ in character from one mixture to another, they indicate that the thermal conductivity of a mixture is not completely determined by the conductivities of its constituents, and by the volume of each constituent present.

The attempts which have hitherto been made to represent the thermal conductivity of glass as a function of its composition and of the unknown conductivities of its constituents, must therefore be considered as not justified by our knowledge of the behaviour of mixtures of substances the conductivities of which are known.

The formula expressing the conductivity of a mixture in terms of its composition and the conductivities of its constituents, must then contain at least one quantity dependent on the characters of the two constituents, and the calculated values of the conductivity may be made to coincide with the observed values at three points. There are many empirical formulæ which under these conditions give values that agree fairly well with the intermediate observations; and although I have found the formula

$$k^n = \frac{p_1 k_1^n + p_2 k_2^n}{p_1 + p_2}, \quad \dots \quad (4)$$

where  $n$  is an arbitrary constant, on the whole satisfactory, the material at our disposal for testing the relative values of the various empirical formulæ which might be suggested, is not yet sufficient to warrant the selection of any one of them as the best representation of the thermal conductivity of a mixture.

The result of this examination may then be summed up as follows:—

Of the three values for the conductivity of a mixture calculated from the mean conductivity, mean resistivity, or mean logarithmic formula, that from the mean conductivity is most unsatisfactory, and that from the mean logarithmic formula least unsatisfactory. The logarithmic formula gives

in general too high, and the resistivity formula too low a value for the conductivity.

The conductivity of a mixture appears not to be dependent solely on the volume and conductivity of each constituent present.

The empirical formula (4) gives a fair representation of the observations in the preceding tables.

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**XXIV. On the Discharge of Electricity through Argon and Helium.** By Hon. R. J. STRUTT, B.A., Scholar of Trinity College, Cambridge\*.

**I**N this paper I propose to describe some observations, partly quantitative and partly qualitative, on electrical conduction through these gases. The observations include measurements of the fall of potential over the negative glow in a vacuum-tube, observations on the luminous effects produced by the discharge, and comparisons of the rate at which ions are produced in them and in air, under the influence of Röntgen rays.

The argon was produced from atmospheric air, the nitrogen being removed by sparking with oxygen in presence of caustic alkali. The surplus oxygen was removed with phosphorus. The helium was extracted from Brazilian monazite-sand by boiling it with sulphuric acid. It was purified in the same way as the argon.

The gases were introduced into the discharge-tubes by the method described by Prof. W. Ramsay (Trans. Chem. Soc. v. 1895, p. 686).

*Measurements of the Cathode-Fall of Potential.*

The investigations of Hittorf and Warburg have shown that when a steady current passes through a gas the difference of potential between the cathode and the outside of the negative glow is a constant, independent of the current passing through the gas, and of the pressure, provided that—

(a) There is no chemical action between the cathode and the gas;

(b) That the negative glow does not cover the whole of the cathode, and is not interfered with by the walls of the tube.

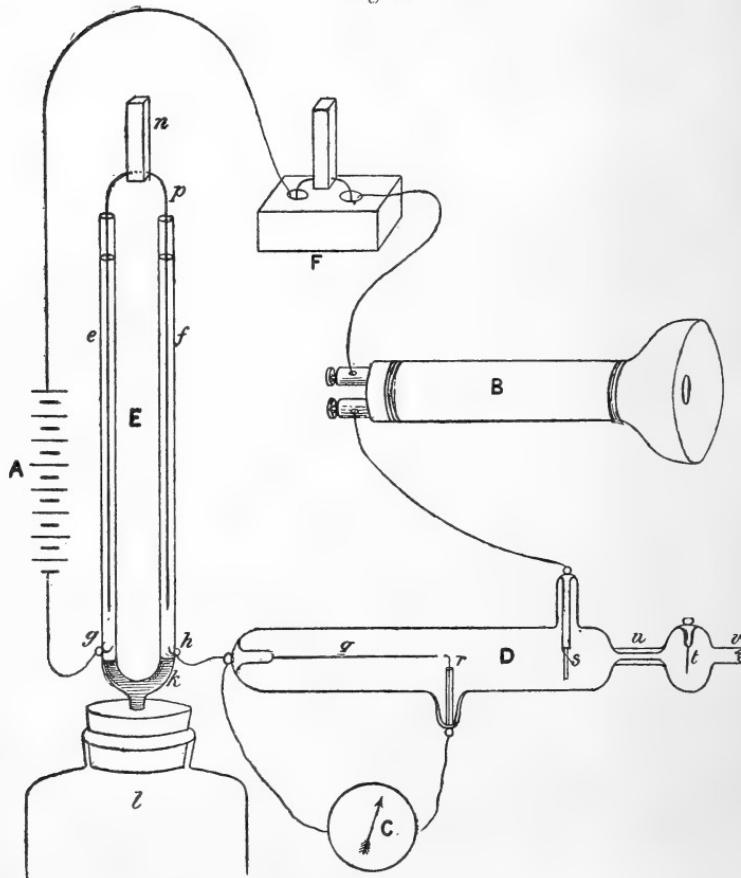
This constant potential-difference is known as the cathode-fall. It is usually of the order of 300 volts, and has a different value for each gas. So far as I am aware, no relation has

\* Communicated by the Author.

yet been found connecting it with other properties of the gas. Indeed the data hitherto available are scarcely sufficient for generalization.

The arrangement I have used for determining the cathode-fall is represented in fig. 1. A is a battery of 400 Planté cells. D is the tube 3 cm. in diameter containing the rarefied

Fig. 1.



gas. The details of this tube are as follows:—*q* is a long platinum wire used as cathode, *r* is a platinum wire which extends to a point 4 or 5 mm. from the end of *q*: *r* is covered with blue enamel-glass except just at the tip. When the current was passing, *r* was outside the negative glow, in the Faraday dark space. The cathode-fall was therefore the difference of potential between *q* and *r*. The exact position

of  $r$  is not important, as the potential-gradient in the Faraday space is small.  $s$  is an aluminium wire, used as anode;  $u$  is a short length of capillary tubing; and  $t$  is a glass bulb into which is sealed another platinum electrode. By using the electrode in  $t$  as anode instead of  $s$ , a discharge could be sent through the capillary tube  $u$ . This was convenient for examining the spectrum of the gas, so as to judge of its purity. An induction-coil was usually used instead of the battery for this purpose, since the discharge obtained with it was much brighter. At  $v$  the vacuum-tube was connected with the arrangement previously described for exhausting and admitting the gas.

$B$  is a telephone, included in the battery-circuit. It is used for ascertaining whether or not the current is continuous. Any intermittence in the current is at once made evident by a singing noise in the telephone.

For measuring the difference of potential between  $q$  and  $r$  one of Lord Kelvin's multicellular voltmeters is used. It is represented diagrammatically at C. The range of this instrument is from 250 to 1000 volts.

In order to test the apparatus and gain experience in using it, preliminary measurements were made on the cathode-fall in hydrogen.

The hydrogen was obtained by the electrolysis of acidulated water; a test-tube full of it was collected and introduced into the vacuum-tube in the way described for helium and argon. At first the measurements obtained were anomalous, being generally very much too high. It was thought at first that the testing electrode was too far from the cathode. The distance was 9–10 mm. The tube was dismounted, and the distance diminished to its present value 4–5 mm. The readings were still erratic, however. Finally the anomaly was traced to the influence of occluded gases in the platinum wire which formed the cathode. These were got rid of by heating the cathode to a bright-yellow heat for some minutes by a strong discharge from an induction-coil. The pump was then worked, and a fresh supply of hydrogen admitted. Readings were now obtained in good agreement with those of previous observers. The mean of these readings was about 298 volts, as against 300 found by Warburg. The agreement is, I think, as good as can be expected.

#### *Cathode-Fall in Helium.*

The tube was exhausted and helium admitted. At first the spectrum of the gas showed traces of nitrogen; an

exceedingly minute quantity would be sufficient to account for this. The nitrogen spectrum was visible only in the positive column, not in the negative glow. The spectrum of the latter showed helium only.

While the gas was in this condition the cathode-fall was at first about 350 volts. The battery-wires were removed and the discharge from an induction-coil sent through the tube, using the aluminium wire *s* as cathode. This wire was strongly heated by the discharge. The aluminium became soft, and fused up into a knob under the influence of surface-tension. At the same time the aluminium spluttered on the walls of the tube. The nitrogen was gradually absorbed by the heated aluminium, and the nitrogen bands faded out from the spectrum. At the same time the cathode-fall, which was observed at intervals, diminished till it reached a value of about 226 volts. The nitrogen was now no longer visible, and the cathode-fall remained stationary.

Since this cathode-fall was below the lowest graduation of the voltmeter, an E.M.F. had to be added to the voltmeter circuit. For this purpose twenty storage-cells were used. Their E.M.F. was independently determined by means of a Cardew voltmeter. This E.M.F. was subtracted from the reading of the multicellular. The first set of readings obtained was as follows:—

265, 268, 271, 265 volts. Mean 267 volts.

Each of these readings was obtained with a different resistance in the main circuit:—

More helium was now admitted. The cathode-fall at once went up to something like 350 volts. But on allowing the discharge from the coil to run for some time, the aluminium absorbed the nitrogen, and the cathode-fall returned to its original value.

Second set of readings:—

265, 268, 271, 272. Mean 267.

The same process was repeated.

Third set of readings:—

270, 265, 270, 265. Mean 267.

The E.M.F. of the battery (20 cells) added in the voltmeter circuit was determined before and after the experiment. The values were the same, 40·7 volts.

Next morning readings were taken with the same sample of gas, to see if the value had altered.

The readings were :—

262, 270, 265. Mean 266.

E.M.F. added 40·0 volts.

The value of the cathode-fall from the mean of all these experiments is

226 volts.

Care was taken in all cases to free the cathode from occluded gases by heating.

No difficulty was found in keeping the telephone silent in these experiments.

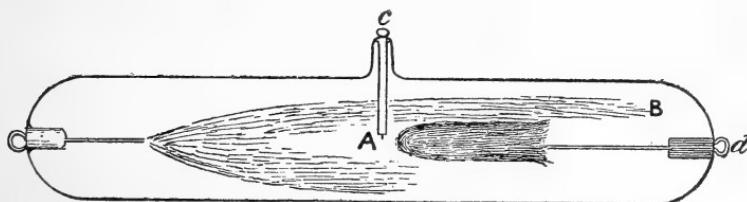
The cathode-fall for helium is not very different from the value 230 volts found for nitrogen by Warburg and others. This may suggest that my helium was contaminated with nitrogen. But I do not think that there is in reality any ground for suspicion. When traces of nitrogen were present, the cathode-fall in the mixture was very much higher than 230 volts; as soon as the spectroscopic test (which is in this case very delicate) showed the absence of nitrogen, the cathode-fall fell to 226 volts.

#### *Cathode-Fall in Argon.*

The determination of the cathode-fall in argon presents peculiar difficulties—difficulties which, so far as I know, have not been encountered in the case of any other gas.

When a wire cathode of the usual form is used, the positive column of the discharge insists on curling round the testing electrode, and going on to the back of the cathode (see fig. 2).

Fig. 2.

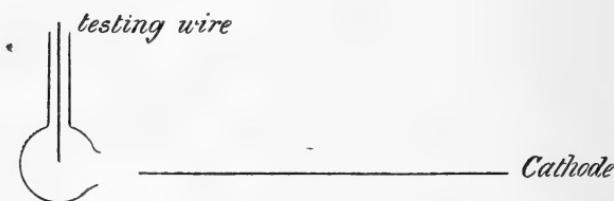


The positive column is represented by the light shading, the negative glow by the dark. The result is that the whole potential-difference, corresponding to the length AB of the positive column, is added on to the cathode-fall measured between the cathode *d* and the testing electrode *c*. The distance to which the extremity B of the positive light

extends depends on the current through the tube. The greater the current, the further it reaches towards the cathode. By increasing the external resistance it can be made to recede as far as the point A. But when this is done the current is so small that it does not suffice to produce a continuous discharge through the gas. The telephone emits a humming noise, and of course no true measurement of the cathode-fall is possible. When the external resistance is diminished so that a continuous current is obtained, the potential-difference between *c* and *d* increases with the current, although the negative glow does not cover the whole cathode. This is due to the added potential-difference of the variable length AB of the positive column.

Many different tubes of various diameters and with the gas at very different pressures were tried, but the same trouble occurred in all. In one tube the testing electrode A was covered with a glass hemisphere open on the side facing the cathode, thus (fig. 3)—

Fig. 3.



It was hoped that this glass protection might keep off the positive column, and enable good measurements to be made; but the readings obtained were just as anomalous as before.

The difficulty was finally overcome in the following manner:— Instead of a wire cathode, a platinum disk was employed, of such a diameter as to fill up as nearly as possible the whole cross-section of the tube without, however, touching the sides. It is clear that in this case the positive column cannot get back behind the testing-point. The negative glow formed a patch on the disk-electrode. The area of this patch depended on the current. And as long as the glow did not cover the whole disk, the cathode-fall was independent of the current. The only objection to the disk is that it is difficult to pass a sufficiently strong current through the tube to heat so large an area satisfactorily. Thus it is difficult to get rid of the occluded gases.

This cause of error vitiated the earlier measurements.

The cathode-fall in argon turned out to be so low that an

E.M.F. had to be added to the voltmeter circuit to bring the readings within the range of its graduations. Larger E.M.F.'s were added in this case than in the case of helium. They were sufficiently large to be determined by the multicellular itself. A key was employed which enabled either the added E.M.F. or the added E.M.F. + the cathode-fall to be measured. By subtraction the cathode-fall was found.

The first set of satisfactory readings was as follows :—

570,	570,	570,	572,	573,	572,
571,	568,	570,	572,		

E.M.F. added 412 volts before readings,  
" " 412 " after "  
Mean value of cathode-fall 159.

A second set of readings on the same sample of gas, made next day, were as follows :—

533,	533,	535,	528,	528,
528,	530,	528.		

Added E.M.F. measured before readings 370,  
" " " after " 365.  
Mean value of cathode-fall 167 volts.

A strong discharge from an induction-coil was now sent through this sample of gas for a considerable time, with a view to removing any traces of nitrogen that might remain by absorption by the sputtered aluminium from the electrode, as in the case of helium.

The readings after this were :—

580,	581,	580,	584.
------	------	------	------

E.M.F. added, measured before readings, 413,  
" " " after " 413.

Cathode-fall 168 volts.

Another sample of argon was next tested. It is not necessary to give the observations in detail, since they resemble closely those given above.

The mean results at first were :—

171 volts.

After prolonged sparking the cathode-fall remained almost unaltered. The observed value was :—

170 volts.

A third sample of the gas gave the value

165 volts.

It was not possible to submit this sample of gas to prolonged sparking owing to an accident, by which air gained admission to the tube.

Taking the mean of all these measurements, we have as the cathode-fall in argon :—

167 volts.

It was mentioned above, p. 293, that one condition for a normal cathode-fall is that there should be no chemical action between the cathode and the gas. This statement is, however, of a somewhat hypothetical nature. It was found by Warburg that the cathode-fall in hydrogen was nearly the same (300 volts) over electrodes of copper, zinc, iron, and platinum. But for aluminium and magnesium cathodes it was much less (about 180 and 160 volts respectively). It seems most natural to attribute the exceptional behaviour of these latter metals to chemical action of the gas, or of traces of impurities in it, upon them. However this may be it appeared to be of interest to determine whether argon would show any similar effect. A few experiments were made to test this point.

A disk cathode of aluminium was employed. It spluttered freely in the argon-filled tube. The values obtained for the cathode-fall were

97, 90, 85.

By continual sparking the value rose somewhat higher. The readings were

100, 105, 105, 115.

The mean value for the cathode-fall in argon over aluminium electrodes is

100 volts.

Thus, so far as these experiments go, the cathode-fall in argon appears to be diminished in the same ratio as that in hydrogen, when aluminium electrodes are substituted for platinum.

#### *Electrodeless Discharge.*

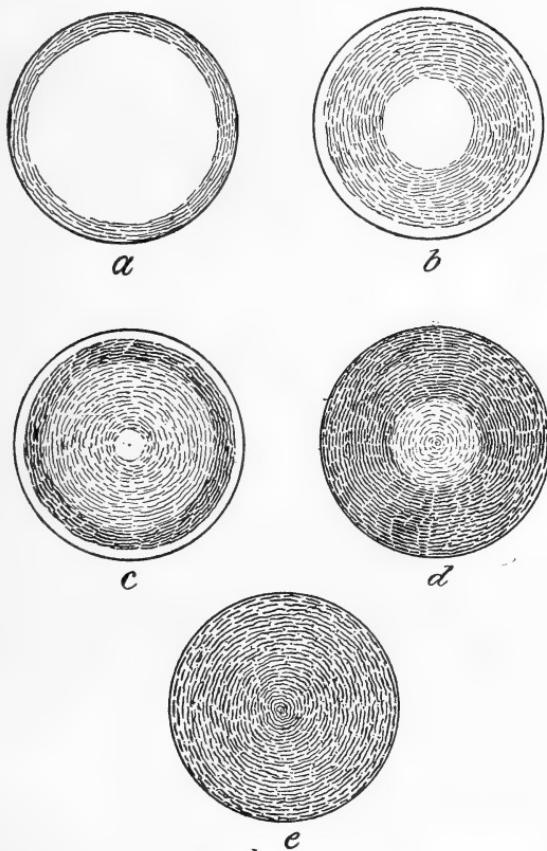
Interesting effects are observed when an endless ring discharge is produced in rarefied argon by discharging a leyden-jar through a coil of wire, inside which a bulb containing the gas is placed. Discharges of this kind have been

investigated by Prof. J. J. Thomson (*Recent Researches in Electricity and Magnetism*, p. 96).

The luminosity in the bulb is confined to the plane of the coil, and is brightest in its outer parts, nearest the wire of the coil. Here the current is most intense.

In argon the phenomena observed are as follows:—As soon as the pressure is low enough to enable the discharge to pass, a thin reddish ring appears in the bulb, just inside the

Fig. 4.



wire coil (fig. 4 *a*). As the pressure diminishes, this red ring broadens out, and a thin ring of bright blue luminosity appears in the outermost part of the bulb (fig. 4 *c*). The blue luminosity is represented by dark shading, the red by light. On further exhaustion this blue ring expands inwards (fig. 4 *d*) until, when the pressure is so low that the discharge has a

difficulty in passing, the blue luminosity fills the entire bulb (fig. 4 e).

The boundary of the blue ring at the stage represented in fig. 4 e is exceedingly definite.

It will be seen from this description that the electrodeless discharge brings out in a very striking way the change from the red to the blue glow in argon first noticed by Sir W. Crookes. The red glow is obtained when the pressure of the gas is high, or when the discharge is feeble. The blue glow is obtained when the pressure is low, or the discharge very intense, as it is in the outer zone of the ring. The bulb remained faintly luminous with a phosphorescent glow after the discharge had been turned off. This glow was observed after a purely red discharge (fig. 4 b) as well as after a purely blue one (fig. 4 e).

The electrodeless discharge in helium does not show any special features. The luminosity is yellow, the D<sub>3</sub> line being prominent.

#### *Conductivity of Helium under Röntgen Rays.*

It is now well-known that gases exposed to Röntgen rays are enabled to conduct electricity. The explanation of this effect is, beyond doubt, that the rays manufacture out of the gas carriers charged with electricity. The motion of these charged carriers or ions under an electromotive force constitutes the current. This kind of gaseous conduction is essentially distinct from the conduction which constitutes disruptive discharge. The former takes place under small E.M.F.'s, the latter, under given circumstances, requires a definite large E.M.F. to produce it. It has been found (see J. J. Thomson, 'The Discharge of Electricity through Gases,' p. 35) that with a given shape of electrodes, and a given distance between them, the current does not increase with the potential-difference beyond a certain point if the radiation is constant. The current becomes "saturated." This occurs when ions are used up in conveying the current as fast as they are produced by the rays.

There is reason to think that the ion conveys the same electric charge, whatever the gas from which it is manufactured (see J. J. Thomson, Phil. Mag. Dec. 1898, p. 543). This being so, it is clear that the ratio of the saturation currents through two gases gives the relative rates at which the rays produce ions in them. Measurements of the relative saturation currents for the common gases have been made (see J. J. Thomson, 'Discharge of Electricity through Gases,' p. 47).

The following is an account of some experiments to determine the ratio of saturation currents in helium and in air :—

The gas was contained in an aluminium cylinder, 2 centim. in diameter (*a*, fig. 5), closed at one end by a sheet of aluminium *b* cemented on. The rays passed in through *b*. The other end was closed by a tightly-fitting cemented plug of ebonite *c*, through which passed a smaller aluminium tube *d*. This last reached nearly to the bottom of the outer cylinder. It served as an inlet for the gas, and also as one of the electrodes. The outer cylinder *a* was used as the other electrode. A glass tube *e* was cemented into *d*, so as to enable a connexion to be made with the mercury-pump, by means of which the air was removed before admitting the helium.

It was found that if the rays fell directly on the ebonite plug *c* the results were very irregular. To guard against this a metal disk was carried on *d* so as nearly to fill up the whole cross-section of *a*, and thus to screen the ebonite from the rays. This screen was of brass, but was faced with aluminium. This was to guard against the abnormal ionization which, as Perrin has shown, occurs at the surface of most metals, but not appreciably at an aluminium surface.

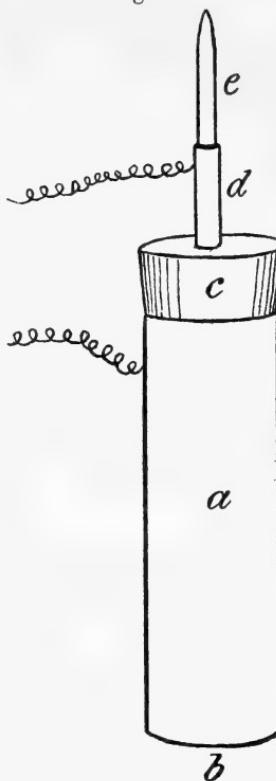
A second precisely similar vessel was provided, which was left full of air, for comparison.

A lead-covered box was used to contain the induction-coil and focus-tube which generated the rays. The two aluminium vessels were arranged side by side so that the rays emerging from holes in the lead box could fall on their ends *b*.

The wires leading to the electrometer from the gas cells were screened by being led through metal tubes connected to earth.

The method of determining the conductivity was to find the rate at which an electric charge could leak through the

Fig. 5.

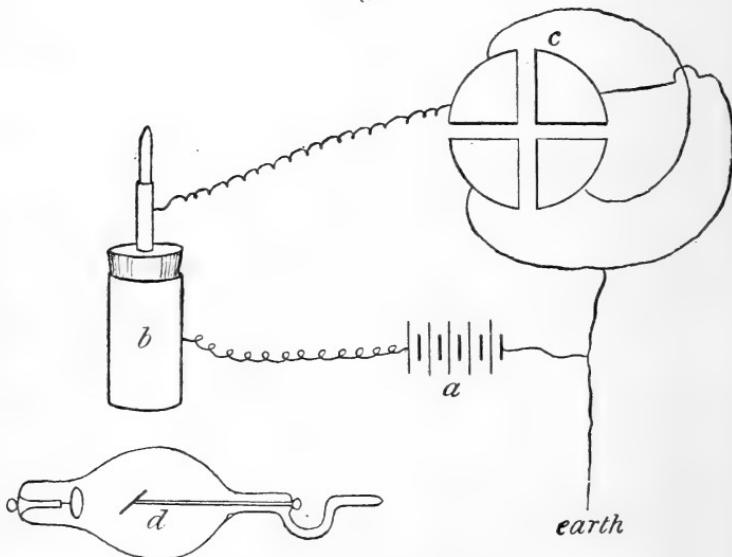


gas to the insulated quadrants of a quadrant electrometer. This rate was first determined when both of the cells were filled with air. The bulb was adjusted to such a position that the rate of leak in each of the cells was very nearly the same. One of the cells was then filled with helium, and the rates of leak again compared. The ratio of these rates was corrected for the slight inequality of the gas cells as determined when both were filled with air.

In this way the relative conductivities were determined.

The electrical connexions are shown in fig. 6.

Fig. 6.



*a* represents the battery (100 cells).

*b*, the cell containing the ionized gas.

*c*, the electrometer quadrant.

*d*, the bulb emitting the rays.

*a* is the battery, consisting of 100 storage-cells. One terminal is put to earth and to a pair of electrometer quadrants. The other terminal to the outside of the cell *b*, containing Röntgenized gas. The central and highly insulated electrode of this cell is connected to the other pair of electrometer quadrants.

Suitable commutating arrangements, consisting of mercury cups in paraffin blocks, are provided for throwing either the air cell or the helium cell into the circuit.

Supposing all to be in working order, the measurements were made as follows:—The two pairs of quadrants were

connected together. The zero was read. The quadrants were disconnected. The rays were turned on for a convenient time, usually twenty seconds. The number of divisions through which the spot of light had moved was observed.

The other gas cell was then substituted and the same process gone through, and so on alternately.

It was first necessary to make sure that the E.M.F. used was sufficient to saturate the gas. For this purpose the rate of leak through the air cell was determined with various E.M.F.'s.

The rays remained on 20 seconds in each case.

No. of Cells.	No. of Divisions passed over in 20 seconds.
5	18
10	27
15	42
20	55
25	67
50	78
100	79

Thus it was found that 100 cells scarcely produced a larger current than 50. Saturation had been reached. In all the subsequent experiments 100 cells were used.

The two cells, both filled with air, were now compared.

The numbers given are the number of divisions passed over in 10 seconds.

Cell No. 1.	Cell No. 2.
53	62
57	59
59	62

Another set of measurements gave the following results :—

Cell No. 1.	Cell No. 2.
50	58
60	65
69	60

The discrepancies between successive readings may be almost entirely attributed to irregularities in the action of the contact-breaker of the coil, and of the high vacuum tube. The measurements following immediately upon one another should be most strictly comparable.

The best method of reducing these results is therefore to

take the average of the ratios of successive readings (coupled by lines in the tables).

The mean ratio of conductivities thus found from the first set of experiments was

$$1 : 1.07.$$

From the second set

$$1 : 1.00.$$

The mean of all these experiments gave as the ratio of the conductivity in cell No. 1 to that in cell No. 2

$$1 : 1.04.$$

Cell No. 2 was then attached to a mercury-pump and exhausted. Helium was admitted to atmospheric pressure. The cell was then carefully readjusted to exactly its original position.

The deflexion produced by 10 seconds' exposure to the rays for each of the cells alternately was noted.

Air (cell No. 1).	Helium (cell No. 2).
32	15
31	13
32	16
32	14

The ratio of conductivities from this last set of experiments is  $1 : 46$ . Other experiments gave results very nearly the same. But in no other case was the radiation quite so steady. I prefer therefore to rely on the above.

Correcting for the inequality of the cells, the ratio is  $1 : 44$ .

It follows that the rate at which ions are produced in helium is about half that at which they are produced in air.

#### *General Remarks.*

The peculiar interest of the gases argon and helium is in their monatomic characters.

The view is now generally taken that the electric discharge is conveyed in all cases by ions, these ions being produced by a dissociation process of some kind. If this be admitted there can be no escape from the conclusion that the ions of monatomic gases are split up into something smaller.

The above experiments make it sufficiently clear, I think, that these gases convey the discharge in a normal manner. If the potential-fall at the cathode is a measure of the energy expended in the ionization of the gas when effected by an

electric field, the experiments show that the ionization of argon and helium is somewhat more easily effected than that of other gases.

There are other reasons for thinking that the atomicity of an elementary gas is not an important factor in its facility of ionization.

Thus mercury vapour was found by Thomson and Rutherford to conduct much more freely than air under the influence of the rays. Helium, on the other hand, conducts only about half as well as air.

There is one peculiarity which seems to belong to monoatomic gases only.

It is only in such gases that aluminium cathodes "splutter." This effect is observed in mercury, argon, and helium.

This, however, is a subsidiary point. There is no means of interpreting it in the present state of our knowledge of the subject.

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*XXV. On an Experiment bearing on the Hypothesis of Electrolytic Convection in Geissler-tubes. By H. MORRIS-AIREY, B.Sc.\**

PROF. J. J. THOMSON, in his book 'Discharge of Electricity through Gases,' describes an experiment to show the convection of chlorine through hydrogen under the influence of an electric discharge.

A small quantity of chlorine is introduced into a capillary tube filled with hydrogen at a low pressure, and the discharge from an induction-coil allowed to take place through the tube. On examining the tube with a spectroscope the chlorine is seen only at the anode, and on reversing the current the chlorine appears at the new anode, and so on as often as the current is reversed.

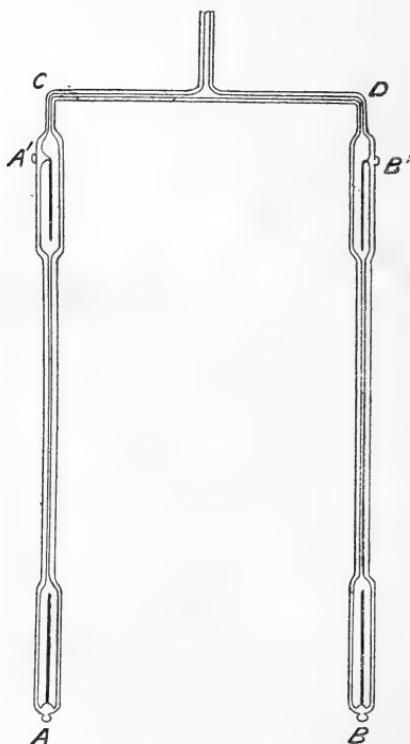
The conclusion Prof. Thomson draws from this is, that the chlorine is actually transported through the hydrogen from one end of the tube to the other after each reversal of the current.

This conclusion, however, does not seem to be justified, since the difference of temperature known to exist at the two electrodes may be sufficient to account for the effect, the chlorine being seen only at the hottest part of the tube. It seemed interesting therefore to see if the motion of the chlorine could be detected in some other way.

An experiment was made with a tube of the shape shown

\* Communicated by Prof. Schuster, F.R.S.

in the diagram, pieces of platinum wire fused into it at the points A, A', B, B' being used as electrodes. Hydrogen and a little chlorine were allowed to enter the tube, and the electrodes A and B connected to the terminals of an induction-coil giving a spark about 6 centim. long.



With a mixture of the gases containing 7 per cent. of chlorine at a pressure of 2 millim. mercury, the spectrum of chlorine was obtained from a small portion of the tube surrounding the anode, while in the rest of the tube no chlorine could be detected. The current was repeatedly reversed, and the effect described by Prof. Thomson observed.

The electrode B was then made the anode, and no chlorine being detected on careful examination of the part AA' the two parts AA' and BB' were fused off at the points C and D whilst the current was still passing.

Making use of the remaining electrodes at A' and B', each of the tubes thus obtained was connected to the induction-coil and examined with a spectroscope.

If Prof. Thomson's theory were correct no chlorine should

have been discoverable in the part AA'. However, the chlorine spectrum was easily obtained from AA'; and on comparison with BB' the intensity of the chlorine lines was found to be the same in both cases. The tubes were fused on again and the experiment repeated, making A the anode, when the same result was obtained.

This proves that if any convection of the chlorine does take place, it is to an extremely small extent, and is certainly not sufficient to account for the effect observed.

To Prof. H. Kayser I wish to acknowledge indebtedness.

Physical Institute, Bonn,  
February 1900.

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**XXVI. On some Novel Thermo-Electric Phenomena.** By  
W. F. BARRETT, F.R.S., Professor of Experimental Physics  
in the Royal College of Science for Ireland\*.

**I**N the course of a determination of some of the physical properties possessed by various new alloys of iron, which had been prepared by Mr. R. A. Hadfield, of Sheffield, I found the thermo-electric behaviour of a particular nickel steel, to which five per cent. of manganese had been added, to be so remarkable that it seemed worthy of a separate note.

The analysis of this alloy (kindly supplied to me by Mr. Hadfield) was as follows :—

Iron .....	68·8	per cent.
Nickel.....	25·0	"
Manganese.....	5·0	"
Carbon .....	1·2	"

The specific electrical resistance of this alloy was found by Mr. Brown and myself to be higher than that of any other alloy we had hitherto examined †. It amounted to no less than 97·52 microhms per cub. centim. (at 15° C.). At the same time its variation of resistance with change of temperature was comparatively small, the temperature-coefficient being 0·08 per cent. per degree C. (between 0° and 250° C.).

The thermo-electric behaviour of the various alloys of iron which Mr. Hadfield had kindly placed in my possession was in course of investigation, and the enormous electrical resistance of this specimen, and of another similar alloy with somewhat less nickel, led me to try earlier than I should otherwise have done some of its other physical properties.

A preliminary experiment was made by coupling a wire of this new alloy successively with different metals and testing

\* Communicated by Prof. G. F. Fitzgerald, F.R.S. From a separate impression of the Trans. Roy. Dublin Soc., vol. vii. pt. v.

† See Trans. R.D.S. vol. vii. pt. 4.

the thermo-electric power of the various junctions up to a red heat. When an iron wire was used as the second metal the thermo-electric force quickly rose till a certain temperature much below redness was reached, and then remained almost stationary, notwithstanding that the temperature of the junction rose from a black up to a bright white heat ; the cool junctions being throughout kept in water at the temperature of the room, or in ice. Here, then, we have the change in the thermo-electric force arrested when a certain temperature is reached, and the force remaining nearly the same in spite of the increasing difference of temperature between the cool and hot junctions. We know that so long as the *difference* of temperature between the cool and hot junctions in most thermo-couples remains constant, and the circuit is unchanged, the potential-difference also remains constant ; but if the difference of temperature between the cool and hot junctions alters, then the potential-difference, as a rule, also changes ; and for *small* changes of temperature the electromotive force thus set up is, in most cases, proportional to the change of temperature. This, of course, is the principle upon which the thermo-electric pile is used as a delicate thermometer ; and with certain alloys this proportionality holds good through a wide range of temperature.

In order to measure the exact temperature of the hot junction, a thermo-electric couple, formed of a platinum wire twisted with a wire of an alloy of platinum containing 10 per cent. of rhodium, was employed. The vapour of boiling water ( $100^{\circ}\text{C}.$ ) and of boiling sulphur ( $445^{\circ}\text{C}.$ ) are the most convenient and reliable fixed points for plotting the lower part of the scale\*. For the higher parts I have used the freezing-point of pure silver ( $961^{\circ}\text{C}.$ ), and of potassium sulphate ( $1066^{\circ}\text{C}.$ ).†.

A reflecting galvanometer was employed, a dead beat high-resistance instrument, of the D'Arsonval type, made by Ducretet, of Paris. Owing to its high resistance the alterations in the resistance of the circuit during the heating and cooling of the couple introduced no sensible error, the deflexions being proportional to the E.M.F. and not to the current.

The value of the scale-reading of the galvanometer in

\* The thermo-couple must, of course, be protected from the sulphur by being enclosed in a hard-glass tube. To obtain the boiling-point of sulphur it is best to employ a hard-glass flask with a long neck, all except the lower portion of the flask being jacketed with asbestos. A convenient arrangement is supplied by the Cambridge Instrument Company ; this I used.

† Heycock and Neville, Trans. Chem. Soc. 1895.

microvolts was accurately determined by means of a standard cell and potentiometer, one scale-division being found to be equal to 26·5 microvolts. With a similar couple Professor Callendar found that the E.M.F. in microvolts at three points ought to be as follows :—

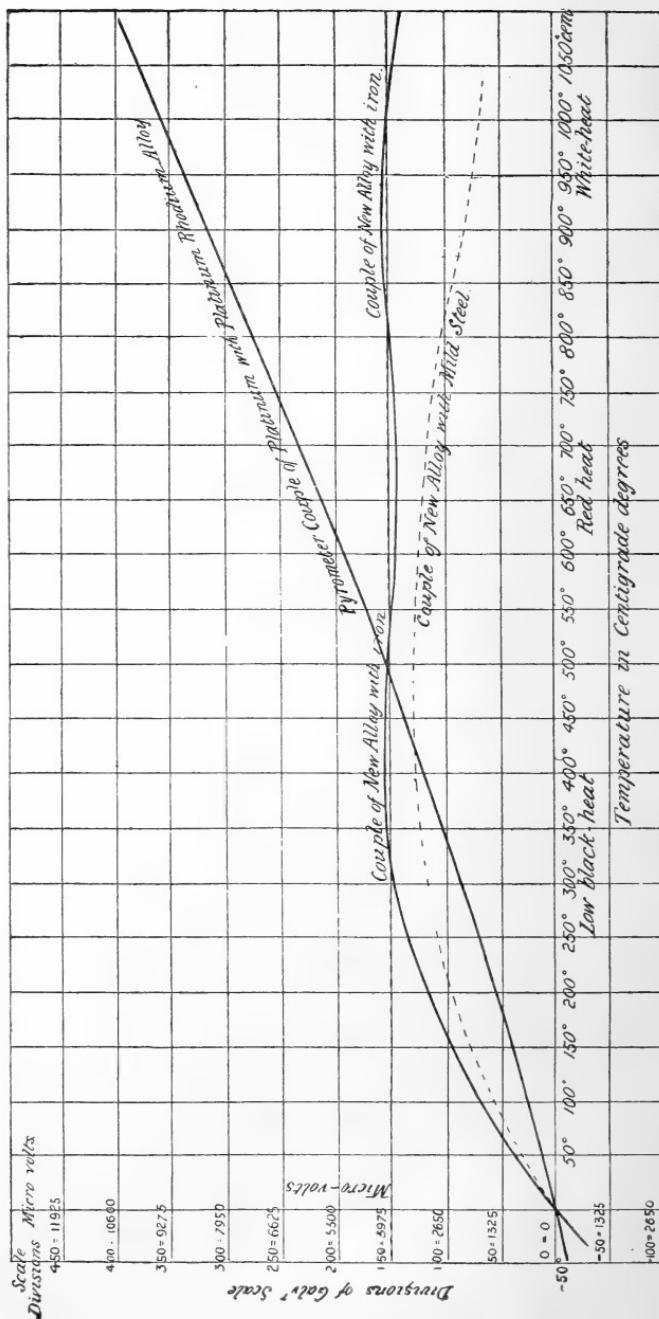
100° C.	.	.	650	microvolts
445°	.	.	3630	"
1000°	.	.	9550	"

the other junctions being in ice. My own determinations at 100° C. and 445° C. gave almost identically the same values in microvolts ; this may be accidental, but the variations of thermo-electric power in different specimens of platinum is probably very slight. I therefore took Professor Callendar's value in microvolts for 1000° C. in preference to the rather different number I obtained\*. The results are plotted in the curve shown in the figure, marked "pyrometer couple."

We will now return to the thermo-electric behaviour of this nickel-manganese-iron alloy. An iron wire, drawn from the purest commercial iron, was coupled with a wire of the alloy. The wires were twisted together at the junction and then brazed. After insulation with asbestos they were lashed alongside of the platinum-rhodium pyrometer couple, and the pair of couples was then inserted in the centre of a thick iron tube held horizontally in, and heated by, a gas furnace, the temperature of which could be raised to a white heat. The cooler junctions of both couples were kept in ice, and pairs of readings were taken as the temperature was raised, and again as it was lowered ; the rise and fall being slow and steady in both cases. As the readings of each couple were taken alternately, to obtain a true comparison three readings were necessary in each case : first, of one couple A ; then, of the other B ; then, of A again ; the mean of the first and last readings of A being comparable with B. The galvanometer being extremely dead-beat, all three readings could be taken closely together. This comparison was repeated two or three times every minute during heating and cooling, thus several series of readings for about every 10° C. rise or fall of temperature were obtained ; the readings which corresponded to similar temperatures in heating and cooling being remarkably concordant, allowance being made for a very small constant difference to be mentioned in the sequel.

\* As (within the limits of the scale) the E.M.F. of the thermo-couple is directly proportional to the scale-readings of the galvanometer, it is easy, when the E.M.F. in microvolts at 100° and 445° C. is found, to determine the higher points in the curve by means of the ratio given above : the scale-readings being plotted as ordinates and the temperatures as abscissæ.

## Thermo-electric Curves of Hadfield's Nickel-Manganese-Steel Alloy.



The results are plotted in the second curve shown on the figure. It will be seen that, up to a temperature of 320° C., the E.M.F. of the nickel-steel alloy and iron couple rose rapidly; it then remained absolutely constant until the temperature rose to 500°, and after this, only a small change occurred up to the highest temperature attainable in the gas furnace employed. The mean E.M.F. between 300° and 1000° C. was in round numbers 4000 microvolts, and the extreme variations from the mean E.M.F. throughout this range of 700° C.—that is, from a low black heat to a white heat—were less than 170 microvolts, or about + and - 4 per cent. of the E.M.F. at 300° C., the cooler junction being kept at 0° C. It will be noticed that there is a slight and curious oscillation of the E.M.F. about the mean line between 300° and 1100° C., the curve cutting the mean E.M.F. at four points, viz., at 310°, 540°, 810°, and 1030° C.

The couple was next exposed to a very low temperature obtained from solid CO<sub>2</sub>, but though a temperature of - 80° C. was reached (the other junction being still kept in melting ice), no other anomalous action occurred, the reverse E.M.F. increasing rapidly as the temperature fell. On again raising the temperature to a white heat, the phenomena previously observed were exactly reproduced, and continued to be so on repeated heating and cooling.

In place of nearly pure iron, other substances were tried as the second metal in conjunction with this alloy. Ordinary commercial iron wire gave a very similar result, the oscillations from the mean E.M.F. being slightly greater. With an ordinary mild steel wire as the second metal, the nickel manganese alloy now gave a different result; this is shown on the lower, dotted curve in the figure. The E.M.F. is less, remains constant only between 400° and 600° C., then begins to fall and continues falling slowly to the highest temperature reached, over 1000° C.

Platinum, copper, and other metals were also tried in conjunction with this alloy, but in no case was there observed the singular constancy of E.M.F. through a wide range of temperature which occurred when iron was the second metal. With platinum the E.M.F. has an opposite sign (to that occurring when the alloy is coupled with iron) up to a temperature of 210° C.; inversion takes place at this temperature, after which the E.M.F. rapidly rises with increasing temperature in an approximately parabolic curve.

A small thermo-electric battery was formed of strips of this alloy with strips of iron, the strips being insulated by asbestos, and brazed at their junctions; 25 of these couples

give an E.M.F. of  $\frac{1}{10}$  of a volt when heated over any flame, the cooler junctions being kept in ice-cold water. A convenient standard of E.M.F. might thus be made if the means of the readings between  $300^{\circ}$  and  $1000^{\circ}$  C. were taken. Whether repeated heating and cooling of the alloy will affect its E.M.F. I cannot say, but I have not yet observed any injury resulting from this cause.

We know so little of the whole subject of thermo-electricity, that the explanation of the remarkable behaviour of this alloy can only be a matter for conjecture. Some light may be thrown on it by the results obtained from the other alloys of iron, when their thermo-electric behaviour is examined. So far I have found that reducing the nickel in the alloy from 25 to 19 per cent., the other constituents remaining the same, does not destroy the sudden arrest of E.M.F. at about  $300^{\circ}$  C.; but the range of temperature where the E.M.F. is nearly constant is less, extending from about  $400^{\circ}$  to  $750^{\circ}$  C.

It has been suggested that the peculiar thermo-electric property of this alloy may be connected with the effect observed by Lord Kelvin, the so-called Thomson effect, whereby a kind of electric convection of heat occurs. It is very possible that it may have some connexion with this, and hence with the *neutral point*, which occurs in the thermo-electric behaviour of certain pairs of metals, such as copper and iron. It is well-known that at a certain critical difference of temperature between the hot and cold junctions of, say, a copper-iron couple, the potential-difference due to heat disappears; as the temperature rises, inversion of the current occurs; and a second inversion may occur at a still higher temperature. In the phenomenon described in this paper, the E.M.F., it is true, does not fall to zero. If, however, the cooler junction were kept at a temperature of  $310^{\circ}$  C., this would be the case; and we should then have a series of three successive small inversions of E.M.F., occurring at  $540^{\circ}$ ,  $810^{\circ}$ , and  $1030^{\circ}$  C. In a copper-iron couple the neutral point is  $275^{\circ}$  C.

I have noticed that the temperature of the neutral point in a copper-iron, or copper-steel couple, is not the same during the *heating* as during the *cooling* of the couple. Moreover, in a couple formed of copper and mild carbon steel, the neutral point becomes lower in successive heatings. Thus, at the *first* heating the temperature of inversion was approximately  $640^{\circ}$  C., and in cooling,  $500^{\circ}$  C.; in the *second* heating,  $550^{\circ}$  C., and in cooling,  $465^{\circ}$  C.; in the *third* heating,  $520^{\circ}$  C., and in cooling,  $465^{\circ}$  C.: the difference between the temperature of inversion in heating and cooling becoming less in each successive heating and cooling. The cool junc-

tion was here at  $16^{\circ}$  C. throughout ; the neutral points at the 1st, 2nd, and 3rd heatings and corresponding coolings of the couple, would therefore be approximately as follows :—

*Neutral Points of Copper-steel Couple.*

	First,	Second,	Third Heating.
When heating ...	$328^{\circ}$	$283^{\circ}$	$268^{\circ}$ C.
When cooling ...	$258^{\circ}$	$241^{\circ}$	$241^{\circ}$ C.

It is obvious therefore that the curve representing the thermo-electric force of a copper-steel couple at different temperatures is not the same for a rising as for a falling temperature. This I have found to be the case with couples formed of several other metals, provided one element of the couple is iron or steel or other alloy of iron. When the other metal is platinum, the difference in the two curves is well seen, though with a platinum-iron couple the difference of E.M.F. in heating and cooling is less marked than with a platinum-steel couple. In the latter case, a considerable area is enclosed by the curves (representing the relation between thermo-electric force and temperature) during heating and during cooling. Hence, at a given temperature, say  $500$  C., of the hot junction, the E.M.F. of a platinum-steel couple is considerably *higher* during heating than during cooling.

The reverse is the case with a couple formed of Hadfield's nickel-manganese-steel and copper, or a couple formed of the same alloy with platinum ; in both these cases at any given temperature, the E.M.F. is *lower* during heating than during cooling. With a couple formed of the same alloy and iron, as described in the earlier part of this paper, there is also a slightly lower E.M.F. at corresponding temperatures during heating than during cooling; but the difference only exists at certain parts of the scale, and is so small that it could not be shown on the curve as reduced in the text. With the nickel-manganese-steel alloy (containing 19 instead of 25 per cent. of nickel) coupled with iron, the E.M.F. is slightly *higher* at corresponding temperatures in heating than in cooling up to the level part of the curve, *i. e.* about  $400^{\circ}$  C., where the E.M.F. becomes almost the same in heating as in cooling—very slightly lower, however,—and remains so until the curve rises, when the E.M.F. again becomes higher at corresponding temperatures in heating than in cooling up to the highest temperature reached : in this case, therefore, the curves showing the E.M.F. during heating and cooling cross each other twice, first at about  $400^{\circ}$  and next at about  $800^{\circ}$  C.

I hope, in a subsequent paper, to give the results of further investigation which I am pursuing on this interesting pheno-

menon, together with the curves for the E.M.F. of various couples during heating and cooling—*thermo-electric hysteresis curves* as they may be called\*. It is very probable that the peculiar thermo-electric deportment of iron, and some of the alloys of iron described in this paper, is intimately associated with the phenomenon of recalescence, or rather of the series of recalescent points which exist in iron and steel.

### XXVII. *On Obliquely-crossed Cylindrical Lenses.*

*By SILVANUS P. THOMPSON, D.Sc., F.R.S.†*

CYLINDRICAL lenses have not claimed much attention from writers on geometrical optics. Certain of their properties, which make them invaluable to the ophthalmic surgeon for the correction of astigmatism, are, however, considered in all modern treatises on ophthalmics. Airy applied them for this purpose, but Donders first treated them systematically, in 1862, in his work *Astigmatismus und cylindrische Gläser*. Reusch in 1868 published his *Theorie der Cylinderlinsen*. Javal has written much on the subject from the ophthalmological point of view, as has Mr. S. M. Burnett. Mr. C. F. Prentice has also written of them in two works, a ‘Treatise on Ophthalmic Lenses’ and ‘Dioptric Formulae for combined Cylindrical Lenses.’ Stokes‡ has proposed a cylindrical lens of variable power by combining at a variable angle two equal cylindrical lenses of opposite sign. The problem of the optical properties of crossed cylindrical lenses was touched upon by Reusch and by Donders. Krüss has written upon the aberration of “bicylindrical” lenses, meaning by that term such lenses as have both surfaces cylindrical and of equal curvature, but with their axes mutually at right-angles. Lastly, Prentice has given very elaborate rules for calculating the equivalent spherocylindrical lens for any combination of two lenses crossed at any angle. The importance of the solution of this problem arises from a point in modern ophthalmic practice:—In cases of ordinary astigmatism in which the refractive

\* As was pointed out by Professor G. F. FitzGerald, F.T.C.D., F.R.S., at the meeting of the Society when this paper was read, the thermo-electric hysteresis here referred to is, no doubt, the cause of the thermo-current which is produced in an iron wire steadily moved through a flame, a phenomenon first noticed and investigated by Dr. F. T. Trouton, F.R.S. See Proc. Roy. Dublin Society, March 1886. I am also greatly indebted to Professor FitzGerald for other suggestions he has made in reading the proof of this paper.

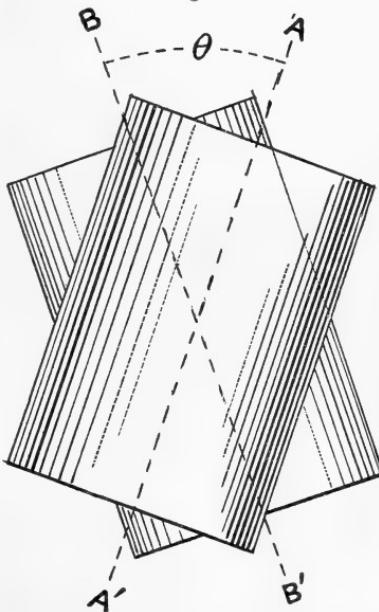
† Communicated by the Physical Society : read Dec. 8, 1899.

‡ Mathematical and Physical Papers, vol. ii. p. 172.

power of the eye is different in different meridians around the optic axis. One process of examination of this defect consists in ascertaining the position of the meridian of greatest refractive power, and in then measuring that power; and, this having been done, measuring the power in a meridian at right angles to the former, that is to say in the meridian of minimum refractive power. The difference between these two powers gives in reality the amount of cylindricity to be corrected. Or the excess of each over the normal spherical refractive power of the eye might be separately corrected by the choice of two appropriate cylindrical lenses which are then superposed at right angles. Sometimes, however, ophthalmic surgeons, whether through insufficient appreciation of the geometrical and optical principles involved, or through some incidental cause, prescribe a lens with two cylindrical curvatures on the respective faces of the lens, not crossed at right-angles but at some oblique angle. As such lenses are difficult of manufacture, and as their optical effect can be precisely reproduced by a suitably calculated and more readily ground spherocylindrical lens, the optician desires to have simple rules for calculating the equivalent spherocylinder. Hence the present attempt to arrive at easier rules for obliquely-crossed cylindrical lenses. To establish these rules it is possible to proceed by a simpler method than that of Reusch, whose investigation is exclusively based upon the properties of parabolic lenses.

2. In the case of thin cylindrical lenses it is customary to call a line drawn through the lens, in a direction parallel to the axis of the generating cylinder of which its curved surface forms a part, "the axis" of that cylindrical lens. Let there be two thin cylindrical lenses placed in contact behind one another, so that their axes A A', B B' make an angle  $\theta$  with one another. The optical axis of the system passes through their intersection and is normal to the plane containing them.

Fig. 1.

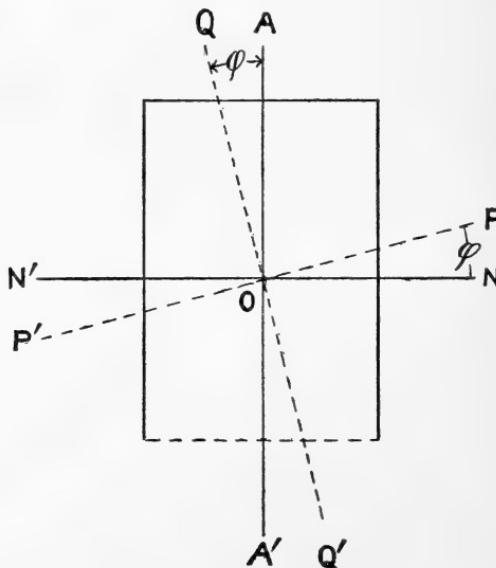


It is required to find the combination consisting of one thin cylindrical lens and one spherical lens which will be the optical equivalent of the system; or, the spherocylindrical lens that is also equivalent. The problem is completely solved when we shall have ascertained the two components, cylindrical and spherical, of the equivalent lens and the angular position of the cylindrical component.

In any lens having at one surface a radius of curvature  $r$ , the curvature which that surface will impress upon a plane wave is  $(\mu - 1)/r$ ; where  $\mu$  is the refractive index of the material. If the lens is cylindrical, having a curvature in one meridian only, the impressed curvature will also be cylindrical; if it be spherical, the impressed curvature of the wave-front will be correspondingly spherical. First approximations only are here considered.

Let (fig. 2)  $A A'$  be the axis of a cylindrical lens, and

Fig. 2.



$NN'$  a line normal to that axis. A plane normal to the axis intersecting the lens in  $NN'$  will have as its trace through the curved surface of the lens a line of the same curvature as the lens, viz.  $\frac{1}{r}$ . Let now an oblique intersecting plane be drawn through the optic axis of the system (*i. e.* the line through  $O$  normal to the plane of the diagram); its intersection  $PP'$  making an angle  $NOP \equiv \phi$  with the line  $NN'$ . The

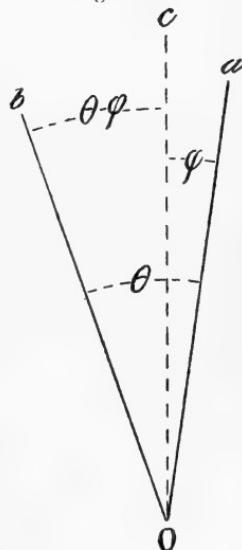
curvature at O of the trace of this plane, where it cuts the curved surface along P P', will be  $\frac{1}{r} \cos^2 \phi$ . This follows from the circumstance that P P' is part of an ellipse whose major and minor axes are respectively  $r/\cos \phi$  and  $r$ . We may further consider the intersection Q Q' of another oblique plane at right-angles to P P'. The curvature at O along the line Q Q' will be  $\frac{1}{r} \sin^2 \phi$ . The sum of these two curvatures will obviously be equal to the original maximum curvature along N N', since the minimum curvature along A A' is zero. Hence we may regard the curvature along N N' as contributing two components of cylindricity of the respective values named in the two directions P P' and Q Q'. If light were admitted through narrow parallel slits set respectively along P P' and Q Q', the convergivity of the two beams respectively impressed by the lens would be  $(\mu - 1) \cos^2 \phi / r$  and  $(\mu - 1) \sin^2 \phi / r$ . If  $r$  is expressed in metres, these two convergivities will be expressed in dioptries according to the practice now internationally adopted by ophthalmists. It is obvious that the angle  $\phi$  may be measured either between N N' and P P', or between A A' and Q Q'.

3. Returning to the problem enunciated with reference to fig. 1, we may now find a solution by resolving each of the two cylindrical lenses into components and then recombining these components in the manner presently to be considered.

Let the line O a (fig. 3) represent the direction of the axis of one of the given cylindrical lenses, having a power of A dioptries, and the line O b the direction of the axis of the other given cylindrical lens of power B dioptries. The angle  $\theta$  between O a and O b is also given. It is required to find the respective number of dioptries C and D of the cylindrical and spherical lenses which shall together constitute a combination whose optical effect is the equivalent of that of A and B. It is also required to find the angular position of the axis of the equivalent cylindrical lens.

It is clear that we might take any line O c through O making an angle  $\phi$  with O a, and take the cylindrical components, along that direction, of the two given cylindrical

Fig. 3.



lenses A and B. The sum of these components would be  $A \cos^2 \phi + B \cos^2(\theta - \phi)$ . Similarly there might be taken, at right-angles to O<sub>c</sub>, the two other cylindrical components, whose sum would be  $A \sin^2 \phi + B \sin^2(\theta - \phi)$ . Now there will be in every case one particular value of  $\phi$  which will make the former sum a maximum and the latter a minimum. If we can find this value of  $\phi$ , the problem is solved.

Differentiating with respect to  $\phi$  the expression above obtained for the sum of the two components along O<sub>c</sub>, and equating to zero, we find that when this sum is a maximum the angle  $\phi$  will be such as to give the relation

$$\frac{A}{B} = \frac{\sin 2(\theta - \phi)}{\sin 2\phi}, \quad \dots \dots \dots \quad (1)$$

to which may be given the alternative form

$$\cot 2\phi = \frac{\frac{A}{B} + \cos 2\theta}{\sin 2\theta}. \quad \dots \dots \dots \quad (2)$$

From this latter  $\phi$  may be reckoned by the aid of trigonometrical tables, A, B, and  $\theta$  being all given. Angle  $\phi$  being thus found, it can be used to calculate the maximum and minimum values, namely the two sums previously expressed. The cylindrical lens representing the maximum sum being set at angle  $\phi$  with the original direction of A, and the cylindrical lens representing the minimum sum being set at  $90^\circ - \phi$ , they will, thus crossed at right-angles to one another, together act as the optical equivalent of the two obliquely-crossed cylinders.

These two rectangularly-crossed cylindrical lenses may again be resolved into the combination of (1) a cylindrical lens, whose axis is along the axis just found for the maximum lens, and of power C dioptres equal to the difference between the maximum and minimum cylindrical powers, and (2) a spherical lens whose power D is that of the minimum. Hence we shall have

$$\begin{aligned} C &= A \cos^2 \phi + B \cos^2(\theta - \phi) - A \sin^2 \phi - B \sin^2(\theta - \phi); \\ C &= A \cos 2\phi + B \cos 2(\theta - \phi), \quad \dots \dots \dots \dots \quad (3) \end{aligned}$$

and

$$D = A \sin^2 \phi + B \sin^2(\theta - \phi). \quad \dots \dots \dots \dots \quad (4)$$

4. The solution thus found is capable of further simplification.

Dividing equation (3) by A, we have :

$$\frac{C}{A} = \cos 2\phi + \frac{B}{A} \cos 2(\theta - \phi).$$

From equation (1) we have

$$\frac{B}{A} = \frac{\sin 2\phi}{\sin 2(\theta - \phi)}.$$

Substituting this in the preceding gives us :

$$\frac{C}{A} = \cos 2\phi + \frac{\sin 2\phi \cdot \cos 2(\theta - \phi)}{\sin 2(\theta - \phi)},$$

$$\frac{C}{A} = \frac{\sin 2\theta}{\sin 2(\theta - \phi)}.$$

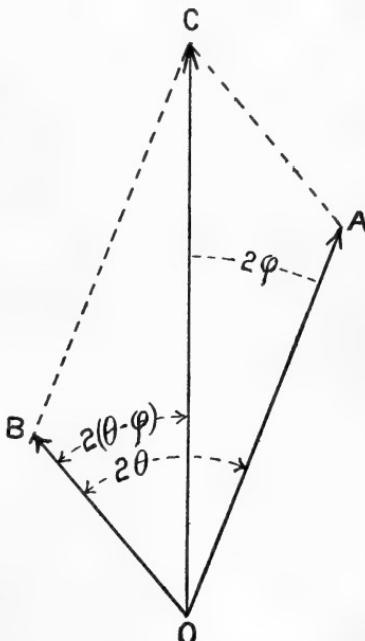
From this immediately follows the relation :

$$\frac{A}{\sin 2(\theta - \phi)} = \frac{B}{\sin 2\phi} = \frac{C}{\sin 2\theta}. \quad \dots \quad (5)$$

This at once suggests that the three magnitudes A, B, and C can be represented by the three sides of a triangle whose respectively-subtended angles are  $2(\theta - \phi)$ ,  $2\phi$ , and  $2\theta$ . Or  $2(\theta - \phi)$ ,  $2\phi$ , and  $\pi - 2\theta$ . In short, the two given cylindrical components A and B may be compounded to find their cylindrical resultant C by means of a parallelogram *in which, however, the angle between A and B is drawn as double the actual angle between the axes of the two given components.*

Hence we obtain the graphic construction of fig. 4. Draw the lines OA, OB to represent, in magnitude only, the powers of the two given cylindrical lenses, and make the angle AOB between them *double* the given angle  $\theta$ . For positive (*i. e.* convergent) cylindrical lenses these directions may be reckoned outwards from the origin, as shown by the arrow-heads. For negative (*i. e.* divergent) cylindrical lenses the directions must be reckoned inwards. Compounding OA and OB in the ordinary way, we obtain the resultant OC which represents in magnitude (and in sign) the resultant cylindrical part of the desired equivalent combination; but the angle AOC will be *double* of the angle that the axis of the resultant cylindrical lens will make with the axis of A.

Fig. 4.



It will then be evident that the value of C is at once calculable directly from A, B, and  $\theta$  by the equation

$$C^2 = A^2 + B^2 + 2AB \cos 2\theta. \dots \dots \dots (6)$$

Having obtained C, the angle  $\phi$  can be most easily calculated by the relation

$$\sin 2\phi = \frac{B}{C} \sin 2\theta. \dots \dots \dots (7)$$

It only remains to find the corresponding expression for the power D of the spherical part of the equivalent combination.

Dividing equation (4) by A we have

$$\begin{aligned} \frac{D}{A} &= \sin^2 \phi + \frac{B}{A} \sin^2 (\theta - \phi). \\ &= \frac{1}{2} \left\{ \frac{\sin 2(\theta - \phi) + \sin 2\phi - \sin 2\theta}{\sin 2(\theta - \phi)} \right\} \\ &= \frac{1}{2} \left\{ 1 + \frac{B}{A} - \frac{C}{A} \right\} \\ &= \frac{1}{2} \frac{A + B - C}{A}, \end{aligned}$$

whence

$$D = \frac{A + B - C}{2}. \dots \dots \dots \dots \dots \dots \dots \dots (8)$$

This last result might also have been obtained by remembering that the maximum power being C + D and the minimum power being D (at right angles), the sum of these, namely C + 2D, will be equal to A + B, whatever the angle between the latter.

An example of the use of the three working formulæ (6), (7), and (8) will suffice.

To find the equivalent sphero-cylindrical combination for the following obliquely-crossed cylindrical lenses :—

$$+3.5 \text{ cyl. ax. } 20^\circ \bigcirc + 2.5 \text{ cyl. ax. } 35^\circ.$$

Here      A = 3.5 dioptres,

B = 2.5 dioptres,

$\theta = 15^\circ$ ,

$\cos 2\theta = 0.866$ ,

$\sin 2\theta = 0.5$ .

By equation (6)

$$\begin{aligned}C^2 &= 12.25 + 6.25 + (17.5 \times 0.866) \\&= 33.65,\end{aligned}$$

whence  $C = +5.8$  dioptres, approximately.

By equation (8)

$$D = \frac{3.5 + 2.5 - 5.8}{2},$$

$$D = +0.1 \text{ dioptres (spherical).}$$

By equation (7)

$$\sin 2\phi = \frac{2.5}{5.8} \times 0.5$$

$$= 0.215,$$

$$\phi = \frac{1}{2} \sin^{-1}(0.215)$$

$= 6^\circ 13'$ , approximately, beyond the position of A.

Hence the equivalent combination would be

$$+ 0.1 \text{ sph.} \bigcirc + 5.8 \text{ cyl. ax. } 26^\circ 13'.$$

5. The circumstance that the cylindrical part of the resultant of two crossed cylindrical lenses varies from maximum to minimum when the angle between the axes of the two lenses is varied from  $0^\circ$  to  $90^\circ$ , suggests a solution to the practical problem how to make a cylindrical lens of variable cylindricity. If two equal positive cylindrical lenses are used, the value of the cylindrical part of their resultant varies from their sum, when the angle  $\theta=0^\circ$ , to zero when the angle  $\theta=90^\circ$ . But while the cylindrical part thus diminishes, in proportion to the square of the cosine of the angle between them, the spherical part of the resultant increases in the proportion of the square of the sine of the same angle. One never obtains a simple cylindrical lens, except in the case of the coincidence of the axes. Similarly if two equal negative cylindrical lenses are used, the resultant consists of a negative cylindrical part and a negative spherical part, the one decreasing, the other increasing when the angle  $\theta$  is increased from  $0^\circ$  to  $90^\circ$ .

Ophthalmists are acquainted with a combination (known as Stokes's lens) consisting of two cylindrical lenses of equal but opposite powers (one a convex, the other an equal concave), arranged to be rotated to various angles of obliquity across one another. When their axes are in coincidence, or  $\theta=0^\circ$ , they neutralize one another completely. When crossed at right-angles their resultant cylindricity is a

maximum but is mixed in sign. Suppose their respective powers were +2 dioptres and -2 dioptres; they will when crossed not act as either a +4 dioptre cylinder, or as a -4 dioptre cylinder, but can be made to act as such by adding at choice either a +2 dioptre spherical lens or a -2 dioptre spherical lens, to neutralize the refractive effects in one or other of the meridians. When crossed at intermediate angles the spherical lens required to neutralize, and so produce the effect of a simple cylinder, would be of some intermediate power. This is a slight inconvenience; but a more serious one exists in the circumstance that in rotating one about the other the axis of the resultant cylindrical effect takes a varying obliquity. This objection is not removed by rotating the two lenses in opposite directions simultaneously.

A more convenient combination to give varying degrees of cylindricity is the following:—Let two lenses be ground, each being a mixed equi-cylinder consisting of a concave and convex ground at right-angles to one another on the opposite faces of the glass. Two such mixed cylinders, if rotated with equal motion in opposite directions, will give a varying cylindricity of fixed direction in space. With the axes of +cylindricity coincident they give the maximum; but when each is rotated to 45°, one to the right, the other to the left, their resultant is zero. In intermediate positions the value of the resultant varies according to the square of the cosine of double the angle through which either has been moved (*i.e.* to the square of the cosine of the angle between their axes), but it remains fixed in direction. When each is rotated beyond 45° they begin again to act as a cylindrical lens, but with the resultant axis of cylindricity negative in the fixed direction in which formerly it was positive. An instrument thus constructed may be graduated so as to be direct-reading.

**XXVIII. *On the Law of Reciprocity in Diffuse Reflexion.***  
*By Lord RAYLEIGH, F.R.S.\**

**I**N the current number of the Philosophical Magazine (vol. xlix. p. 199) Dr. Wright discusses the question of the amount of light diffusely reflected from a given area of a matt surface as dependent upon the angle of incidence ( $i$ ) and the angle of emission ( $\epsilon$ ). According to Lambert's law the function of  $i$  and  $\epsilon$  is

$$\cos i \cos \epsilon; \dots \quad (1)$$

and this law, though in the present case without theoretical

\* Communicated by the Author.

foundation, appears approximately to represent the facts. The question may indeed be raised whether it is possible so to define an ideally matt surface that Lambert's law may become strictly applicable.

The conclusion drawn by Dr. Wright from his experiments with compressed powders upon which I desire to comment is that numbered (4) in his *résumé* of results, viz. "A law for the intensity of reflected scattered light cannot be symmetric in reference to  $i$  and  $\epsilon$ ." It appears to me that this statement is in contradiction to a fundamental principle of reciprocity, of such generality that escape from it is difficult. This principle is discussed at length in my book on the 'Theory of Sound,' § 109. Its application to the present question may be thus stated:—Suppose that in any direction ( $i$ ) and at any distance  $r$  from a small surface (S) reflecting in *any manner* there be situated a radiant point (A) of given intensity, and consider the intensity of the reflected vibrations at any point B situated in direction  $\epsilon$  and at distance  $r'$  from S. The theorem is to the effect that the intensity is the same as it would be at A if the radiant point were transferred to B\*. The conclusion follows that whatever may be its character in other respects, the function of  $i$  and  $\epsilon$  which represents the intensity of the reflected scattered light *must* be symmetrical with respect to these quantities.

The actual departures from the reciprocal relation found by Dr. Wright were not very large, and they may possibly be of the nature of experimental errors. In any case it seems desirable that the theoretical difficulty in accepting Dr. Wright's conclusion should be pointed out.

## XXIX. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 158.]

December 20th.—W. Whitaker, B.A., F.R.S., President,  
in the Chair.

THE following communications were read:—

1. 'On some Effects of Earth-movement on the Carboniferous Volcanic Rocks of the Isle of Man.' By G. W. Lamplugh, Esq., F.G.S., of H.M. Geological Survey.

The author, since the completion of his survey of the Isle of

\* I have not thought it necessary to enter into questions connected with polarization, but a more particular statement could easily be made.

Man, has studied the coast-section in the Carboniferous volcanic series between Castleton Bay and Poolvash, with the result that he has discovered evidence that the strata have undergone much deformation in pre-Triassic times. In the western part of the outercrop the volcanic material consists almost wholly of tuff, in places bedded and fossiliferous; in the eastern part exists a chaotic mass of coarse and fine fragmental volcanic material, traversed by ridges of basaltic rock and containing entangled patches of dark limestone. The author now considers that the larger lenticles and most of the smaller blocks of limestone have been torn up from the underlying limestone-floor during a sliding forward or overthrusting of the volcanic series upon it. Such blocks do not contain ashy material, though patches of truly interbedded, ashy limestone are probably also present. The sections at Scarlet Point, Poolvash, and between Cromwell's Walk and Close-ny-Chollagh Point are described and figured. Strips of limestone are found to shoot steeply upward and become wedged in between the blocks in the agglomerate; they give indications of sliding and disturbance, and their outer surfaces are indurated and chert-like. The ash, which usually rests on black argillaceous limestone-flags, in places appears to come into juxtaposition with a somewhat lower horizon, crushed, platy material intervening between the two. Steep domes of the limestone break into sharp crests, which shoot up into the ash and are bent over towards the north; and between the crests small ragged strips of limestone are entangled among the tuff. Bands of vesicular basalt are bent and shattered. A dyke-like mass has had a segment sliced off and thrust forward among the agglomerate, so that its flow-lines of vesicles are sharply truncated along the fractured edge, which is often notched and filled in with ash as though lumps had been torn out of it. The composition of the included masses is influenced by the neighbourhood of the rocks *in situ*, being calcareous near limestone, and basaltic near the basalt-masses.

The phenomena may be explained as the effects of earth-movement on a group of rocks consisting of limestone passing up into tuff, interbedded with lava-flows, and possibly traversed by sills or dykes of basaltic rock. The results of the disturbance appear to be limited vertically and horizontally, and to have been determined by the differential resistance of the component rocks. Analogous features occur in the Borrowdale Volcanic Series and in the Silurian volcanic rocks of Portraine.

2. ‘The Zonal Classification of the Wenlock Shales of the Welsh Borderland.’ By Miss Gertrude L. Elles.

This paper deals with the Wenlock rocks of Builth, the Long Mountain, and the Dee Valley, and establishes the following sequence in these districts:—

BUILTH.	LONG MOUNTAIN.	DEE VALLEY.	SOUTHERN SWEDEN.
Lower Ludlow.	Lower Ludlow.	Nant-Glyn Flags.	Cardiola-Shales.
(f) 6. Zone of <i>Cyrtograptus Lundgreni</i> , Tullb.	Zone of <i>C. Lundgreni</i> .		Zone of <i>C. Carruthersi</i> , Lapw. = Zone of <i>M. testis</i> .
(e) 5. Zone of <i>Cyrtograptus rigidus</i> , Tullb.	Zone of <i>C. rigidus</i> .		Moel Ferna Slates. } Zone of <i>C. rigidus</i> .
(d) 4. Zone of <i>Cyrtograptus Linnarssoni</i> , Lapw.	Zone of <i>C. Linnarssoni</i> .	Moel Ferna Slates. } Zone of <i>C. Linnarssoni</i> .	
(c) 3. Zone of <i>Cyrtograptus</i> , sp. nov.	?	Pen-y-glog Grit.	Zone of <i>M. riccartonensis</i> .
(b) 2. Zone of <i>Monograptus riccartonensis</i> , Lapw.	Zone of <i>M. riccartonensis</i> .	Pen-y-glog Grit. } Zone of <i>M. riccartonensis</i> .	
(a) 1. Zone of <i>Cyrtograptus Murchisoni</i> , Carr.	?	Pen-y-glog Grit. } Zone of <i>C. Murchisoni</i> .	Zone of <i>C. Murchisoni</i> .
(Local Unconformity.) Tarannon Shales?	(Local Unconformity.) Purple Shales (? Tarannon). Llandovery Grits.	(Succession conformable.) Tarannon Shales. Corwen Grit.	(Succession conformable.) Shales with graptolites.
Llandovery Grits.			

The results obtained by the author completely confirm the work of Tullberg on the Wenlock Shales of Southern Sweden.

Along the Welsh Border the Wenlock rocks do not cover a large area, but are merely a fringe to the Ludlow rocks. The former are characterized by graptolites of the *priodon-Flemingii* type, the latter by those of the *colonus*-type.

The general structure of the Builth district is a syncline towards the north and north-west, part of a series of folds whose axes run north-east and south-west. A later set of movements, along east-and-west axes, and of later date, lifted the district to the north and north-west of Builth, and, combined with the effect of previous movements and subsequent denudation, caused the exposure in the north and north-west of beds which are overlapped to the east. The full six zones in the foregoing table occur to the north-east of Builth-Road Station, but some of them are overlapped north-west of Builth; and at Aberedw Hill, east of Builth, only the highest zone is exposed. The entire succession in the northern and north-western part of the district is given below:—

<b>Ludlow</b> <b>Wenlock</b> <b>Shales</b>	<table border="0"> <tbody> <tr> <td>10. Hard light-grey siliceous flags.</td><td></td></tr> <tr> <td>9. Micaceous sandy shales, with rotten limestone bands.</td><td></td></tr> <tr> <td>8. Calcareous flagstones, with fossiliferous bands.</td><td></td></tr> <tr> <td>(f) 7. Calcareous fissile shales, with beds of flagstone. =Zone of <i>Cyrtograptus Lundgreni</i>.</td><td></td></tr> <tr> <td>(e) 6. Hard grey calcareous shales with graptolites. =Zone of <i>Cyrtograptus rigidus</i>. Feet.</td><td></td></tr> <tr> <td>5. Light-coloured flags, unfossiliferous .....</td><td>(400 ?)</td></tr> <tr> <td>(d) 4. Grey calcareous flags and shales, with limestone-concretions .....</td><td>300 =Zone of <i>Cyrtograptus Linnarssoni</i>.</td></tr> <tr> <td>(c) 3. Soft shales with harder flaggy beds .....</td><td>200 =Zone of <i>Cyrtograptus</i>, sp. nov.</td></tr> <tr> <td>(b) 2. Hard calcareous flagstones .....</td><td>300 =Zone of <i>Monograptus riccartonensis</i>.</td></tr> <tr> <td>(a) 1. Soft fissile shales alternating with flags. =Zone of <i>Cyrtograptus Murchisoni</i>.</td><td></td></tr> </tbody> </table>	10. Hard light-grey siliceous flags.		9. Micaceous sandy shales, with rotten limestone bands.		8. Calcareous flagstones, with fossiliferous bands.		(f) 7. Calcareous fissile shales, with beds of flagstone. =Zone of <i>Cyrtograptus Lundgreni</i> .		(e) 6. Hard grey calcareous shales with graptolites. =Zone of <i>Cyrtograptus rigidus</i> . Feet.		5. Light-coloured flags, unfossiliferous .....	(400 ?)	(d) 4. Grey calcareous flags and shales, with limestone-concretions .....	300 =Zone of <i>Cyrtograptus Linnarssoni</i> .	(c) 3. Soft shales with harder flaggy beds .....	200 =Zone of <i>Cyrtograptus</i> , sp. nov.	(b) 2. Hard calcareous flagstones .....	300 =Zone of <i>Monograptus riccartonensis</i> .	(a) 1. Soft fissile shales alternating with flags. =Zone of <i>Cyrtograptus Murchisoni</i> .	
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The Wenlock Shale of this area was deposited on the sinking shore-line of the old Llandeilo ridge, resulting in the overlap of higher beds on lower.

The Long Mountain is a syncline with a north-east and south-west axis. Here also there must have been deposition on a sinking ridge accompanied by overlap. The lowest beds, exposed near Chirbury, belong to the zone of *Monograptus riccartonensis*; but on the north-west side, near Middletown, the lowest beds seen above the Tarannon Shales belong to the zone of *Cyrtograptus Linnarssoni*. The relationship of these beds to the Tarannon Shales is regarded as an unconformity. The sections in this district confirm those established for the Builth area.

In the Llangollen Basin the general structure is a synclinal fold complicated by many minor folds and faults. The 'Pale Slates' are covered by darker shales belonging to the zone of *Cyrtograptus Murchisoni*; and in this district the relationships of the lowest zones are clearer than at Builth or the Long Mountain.

The palaeontological part of the paper describes several species, some of which are recorded for the first time in the country: *Cyrtograptus Curruthersi*, *C. rigidus*, and a new species of *Cyrtograptus* of zonal value, four varieties of *Monograptus Flemingii*, three of *M. vomerinus*, one variety of *M. testis*, and two new species of *Monograptus* are among the forms dealt with.

3. 'On an Intrusion of Diabase into Permo-Carboniferous Rocks at Frederick Henry Bay (Tasmania).' By T. Stephens, Esq., M.A., F.G.S.

The relationship of the abundant diabase to the Permo-Carboniferous strata of the island has been long a matter of dispute. Among others, Jukes described sections which appeared to confirm the view that Permo-Carboniferous sediments were deposited round vast masses of igneous rock previously cooled and denuded. The author has identified and visited the sections, and finds in one that, although there is a step-like junction between the sediments and the igneous rocks, it is the result of the intrusion of diabase, and not of the deposition of sediment. The sediment, which is fossiliferous, is converted into an intensely hard whitish marble, and the associated shale-bands into chert. The diabase, which is ordinarily an ophitic rock, acquires at the junction a finely crystalline-granular texture. Jukes's second section also gives undoubted evidence of intrusion.

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PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

APRIL 1900.

XXX. *On the Change of Volume and of Length in Iron, Steel, and Nickel Ovoids by Magnetization.* By H. NAGAOKA and K. HONDA\*.

IN our former paper † we have described some effects of magnetization on the dimensions of nickel and iron, as well as those of hydrostatic pressure and longitudinal pull on the magnetization. We have shown that there is reciprocal relation between the two, and that the Villari effect in iron is a natural consequence of the observed changes of dimensions. Unfortunately the range of the magnetizing-field was limited to a few hundred c.g.s. units, so that the investigation of the behaviour of these metals in high fields was reserved for further experiments. In addition to this, the ferromagnetics were not of the shape to be uniformly magnetized, with the exception of iron ovoids. It was therefore thought desirable to repeat the experiment on ovoids of ferromagnetic metals, and to extend the investigation into still stronger fields.

In his well-known researches on the changes of dimensions of iron and other metals by magnetization, Bidwell ‡ pushed the field-strength to 1500; in the present experiment the field-strength is greater than that of Bidwell by 700. In addition to ordinary soft iron and steel ovoids, wolfram steel, from Bohler, in Vienna, was tested, with a result which

\* Communicated by the Authors.

† Nagaoka & Honda, Phil. Mag. vol. xlvi. p. 262 (1898).

‡ Bidwell, Phil. Trans. vol. clxxix, p. 205 (1889).

330 Messrs. Nagaoka and Honda on Change of Volume and showed a remarkable difference from ordinary steel as regards the change of dimensions wrought by magnetization. As was generally supposed, the change of volume is very small in iron and nickel in weak fields, but with strong magnetizing-force the effect becomes generally pronounced.

#### *Method of Experiment.*

The same apparatus as before described was used in measuring the change of length and of volume. A small alteration was made in the arrangement of the magnetizing-coil. Owing to the strong magnetizing-current, a special arrangement was provided for keeping the interior of the coil at constant temperature. A double-walled tube of brass was inserted in the coil, and a constant stream of cold water was passed in the interspace for more than an hour before each experiment. As the resistance of the coil was only 0·56 ohm, the rise of temperature was so small that the ferromagnetic placed in its core was scarcely affected. The change of length was measured by means of an optical lever, as before described \*. For measuring the change of volume, the ovoid was sealed in a glass tube with capillary neck (internal diameter about 0·4 mm.), and so placed in the tube that it rested in the axial line, and never came in contact with the wall of the tube. The magnetizing-coil and the tube were placed horizontal. The motion of the meniscus was measured by a microscope provided with micrometer ocular. For the minute particulars we must refer the reader to the former paper on magnetostriction.

The following are the dimensions of ovoids used in the present experiments :—

Specimen No.	Metal.	$\alpha$ (cm.).	$c$ (cm.).	$v$ (c.cm.).	$\rho$ .	N.
1	Nickel.....	0·750	12·50	31·50	8·86	0·125
2	"	0·500	10·00	10·48	8·86	0·0848
3	Soft Iron .....	0·750	12·50	31·45	7·84	0·125
4	"	0·500	10·00	10·53	7·83	0·0848
5	Ordinary Steel	0·750	12·50	31·60	7·83	0·125
6	"	0·500	10·00	10·57	7·81	0·0848
7	Wolfram Steel	0·750	12·50	31·82	7·90	0·125
8	"	0·500	10·00	10·53	7·95	0·0848

\* Nagaoka, Phil. Mag. vcl. xxxvii. p. 131 (1894); Wied. Ann. Bd. liii. p. 487 (1894).

*a* gives the semi-minor axis, *c* the semi-major axis, *v* the volume,  $\rho$  the density, and *N* the demagnetizing factor of the ovoids. The volume of each specimen was measured by weighing the ovoids in water.

The elastic constants of these metals were measured by flexure and torsion experiments on rectangular prisms made from the same specimens as the ovoids. The prisms were 14·6 cm. long and 0·896 cm. sq. in cross-section. *E* gives Young's modulus, *K* ( $=n$ , using Lord Kelvin's notation) the modulus of rigidity, and  $\theta$  the constant defined by the equation

$$\frac{E}{2} \left( \frac{1+2\theta}{1+3\theta} \right) = K.$$

Metal.	<i>E</i> (c.g.s.).	<i>K</i> (c.g.s.).	$\theta$ .
Nickel.....	$2 \cdot 07 \times 10^{12}$	$0 \cdot 771 \times 10^{12}$	1·082
Soft Iron .....	$2 \cdot 10 \times 10^{12}$	$0 \cdot 800 \times 10^{12}$	0·844
Steel .....	$2 \cdot 04 \times 10^{12}$	$0 \cdot 838 \times 10^{12}$	0·384
Wolfram Steel ...	$2 \cdot 02 \times 10^{12}$	$0 \cdot 849 \times 10^{12}$	0·306

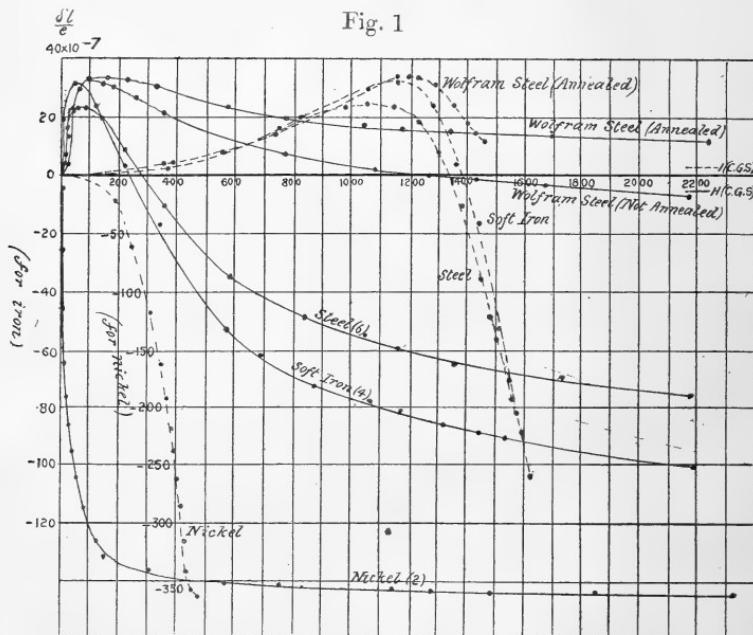
The magnetization of each of these ferromagnetics was determined by the magnetometric method, after the ovoids had been carefully annealed, with the following results :—

Nickel (2).		Soft Iron (4).		Steel (6).		Wolfram Steel (8).	
H.	I.	H.	I.	H.	I.	H.	I.
0·7	24·2	1·0	62	1·9	23	2·7	18
1·4	49·8	2·5	160	2·4	44	6·8	65
3·0	138·6	4·3	291	6·9	183	12·6	193
5·4	238·0	9·5	587	9·7	279	20·2	498
10·9	336·8	12·7	750	13·1	385	25·8	748
37·8	395·7	19·9	948	23·3	651	44·5	992
74·1	420·0	37·2	1111	32·3	815	83·6	1116
125·3	434·5	99·6	1255	50·2	984	118·0	1170
171·6	438·7	155·5	1309	116·3	1196	191·0	1224
240·3	440·7	270·3	1400	174·4	1260	344·6	1301
481·4	443·4	433·6	1479	345·0	1379	512·3	1348
674·2	444·5	584·6	1520	520·2	1440	666·6	1373
914·0	446·8	792·8	1546	873·7	1489	940·3	1400
1233·0	447·7	992·6	1562	1149·8	1512	1213·3	1423
1747·0	448·7	1585·8	1607	1822·6	1549	1674·9	1452

*Iron* (fig. 1).—The change of length experienced by soft iron is too well known to need any description. The ovoid elongates in weak fields till it attains a maximum, being longer by about 3 to 4 millionths of its initial length; it then decreases in length, and becomes shorter than in the unmagnetized state. The contraction goes on gradually increasing, and in the present experiment it does not seem to reach an asymptotic value, even in fields of 2200 c.g.s. units, where the contraction amounts to about  $\frac{1}{100,000}$ . The present result agrees qualitatively with Bidwell's experiment, but the contraction is much greater. The discrepancy is probably to be accounted for by the difference of shape.

*Steel* (fig. 1).—Ordinary steel behaves just like iron, the difference being the smallness of elongation and contraction, and the field at which the elongation vanishes lies in the stronger. The field of maximum elongation for wolfram steel is greater than for ordinary steel or iron, and that of no elongation in the unannealed state is several times greater than for iron or ordinary steel. Such a field corresponds to

Fig. 1



$H=1200$ . When the wolfram steel is annealed the retraction after reaching the maximum takes place very slowly, and the

characteristic as regards the field of no elongation becomes exceedingly pronounced. From the curve of length-change it does not appear that it will ever cut the line of no elongation, even in intense fields.

*Nickel* (fig. 1).—The behaviour of an annealed nickel ovoid is nearly the same as observed by one of us. With increasing field the contraction reaches an asymptotic value, which in the present case is greater than Bidwell's result, obtained from experiments on a nickel wire. This discrepancy is to be sought partly in the difference of shape, and partly in the difference of treatment, as will be clearly illustrated by experiments on the change of volume. We have also reason to believe that repeated annealing alters the elastic behaviour of ferromagnetics as regards the strain wrought by magnetization.

The curves of elongation in iron and nickel plotted against the intensity of magnetization are given by dotted lines in fig. 1. The change of length at first takes place very slowly, but on reaching saturation the rate of change becomes very rapid. So far as the present experiment goes, the rate does not diminish except in annealed wolfram steel, in which we notice a slight flattening. In nickel we find a slight bend when the magnetization becomes saturated.

#### *Change of Volume by Magnetization.*

Experiments by several physicists prove that magnetization produces change of volume in ferromagnetics, in contradiction to the popular belief, which is based on Joule's experiment. The alteration of volume accompanying the magnetization of ferromagnetics is generally very small in weak fields; but, as will be seen from the present experiment, the phenomenon is more marked as the field is made stronger. As we have already remarked, the change of volume as measured by Cantone \* with an iron ovoid must have been exceedingly minute, as the magnetizing field was very small. Dr. Knott † has published several papers on the change of internal volume of ferromagnetic tubes, showing that iron, nickel, and cobalt are subject to the change by magnetization. As our result regarding the same question was somewhat different, especially in the case of nickel, we have thought it advisable to settle the discrepancy by fresh experiments.

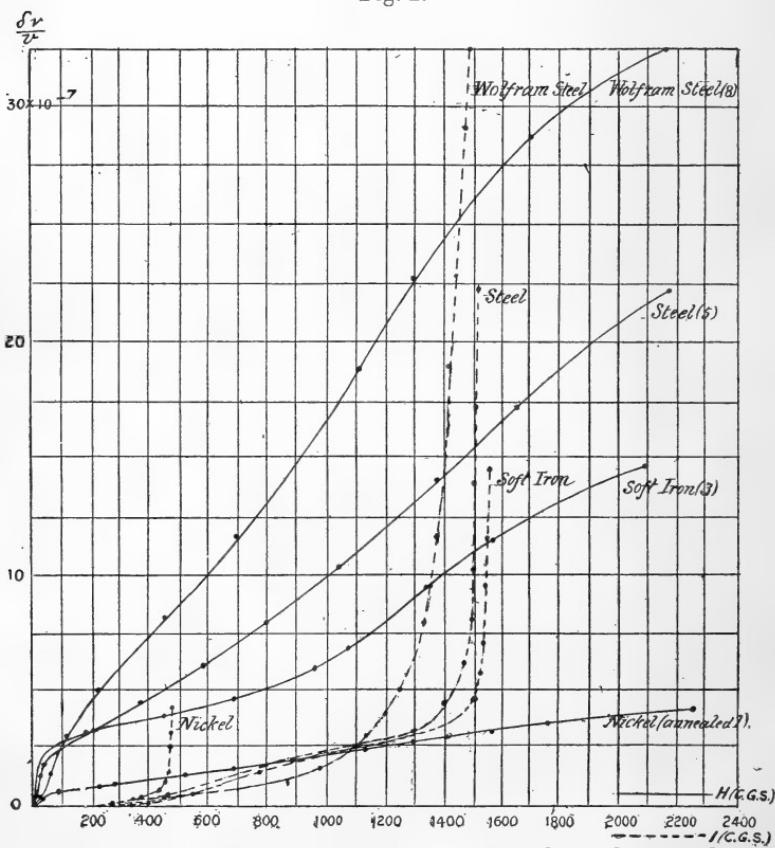
*Iron and Steel* (fig. 2).—Preliminary experiments on an iron ovoid showed that there is considerable increase in the

\* Cantone, *Mem. d. R. Accad. d. Lincei*, tom. vi. p. 487 (1891).

† Knott, *Trans. Roy. Soc. Edin.* vol. xxxviii. p. 527 (1896); vol. xxxix. p. 457 (1898).

volume-change as the ovoid is annealed. The increase becomes more significant as the field is made stronger. In steel, the effect of annealing is greater than in iron. In strong fields the volume-change of the annealed steel ovoid is nearly twice as great as in the unannealed state. Wolfram steel is very little affected by annealing as regards the volume-change, but the change itself is several times greater than in nickel or iron. In fact, the motion of the capillary meniscus in the dilatometer can be easily followed by the naked eye. Curves given in fig. 2 are plotted from measurements made on annealed ovoids.

Fig. 2.



*Nickel* (fig. 2).—As specimens of nickel almost always contain traces of iron, the change of volume will probably depend on the chemical nature. In addition to this, the mechanical process which the metal underwent before it was brought to a form suitable for experiment must have sub-

stantially altered its elastic behaviour. The nickel rod which we used in the former experiment was hammered from a nickel plate to a prism of square cross-section. It contained 1·75 per cent. of iron, besides traces of manganese and carbon. The ovoids used in the present experiment were prepared from a thick plate, and were nearly pure nickel, the quantity of iron which was present as impurity being immeasurably small. As the material is likely to become homogeneous by repeated annealing, the ovoids were carefully annealed for about 50 hours. The ovoid was wrapped with asbestos and placed in a thick metal tube, the interspace between the ovoid and the wall of the tube being filled with fine charcoal powder. The tube was then placed in a charcoal fire. When the ovoid was annealed in this way, there was some trace of oxidation on its surface. The change of volume after each annealing was examined, with a result that the process of annealing increases the effect. It therefore appears that the previous history of the specimen exercises an important influence on the magnetization and on the dimensions of ferromagnetics as affected by magnetization. The anomaly in the length-change noticed by Bidwell in two specimens of nickel wire is probably not the effect of temperature, but is to be ascribed to the cause above stated. In contradiction to our former result with a square prism, the ovoid showed increase of volume. The amount of increase was small compared with the decrease noticed in the previous experiment. Cantone \* obtained tolerably large increase of volume in a nickel ovoid ; our former result was nearly half as large, while in the present experiment there is a slight increase. The discrepancy is probably due to the difference of treatment before the specimen was turned to the proper shape for experiment, and also to its chemical composition.

The volume-change of ferromagnetics considered as a function of the magnetizing field takes place very slowly in weak fields ; it then increases in a more rapid ratio till it reaches the 'Wendepunkt' ; then the change becomes slower, but goes on increasing nearly in a straight line. Up to  $H=2000$  there is no tendency to decrease in the rate of change. With a still stronger field, the increase of volume will probably become more considerable.

In our former experiment, the range of the magnetizing force was confined to a few hundred c.g.s. units. In the present experiment, the increased field-strength unveiled the character of the change of volume considered as a function of

\* Cantone, *Atti d. R. Accad. d. Lincei*, tom. vi. p. 257 (1891).

the intensity of magnetization. As will be seen from the curves (dotted lines in fig. 2), the increase in nickel and steel takes place quite slowly before the magnetization reaches saturation. As soon as the magnetization reaches this state, the increase becomes very rapid, so that the branch of the curve ascends nearly parallel to the axis of volume increase. There we find that a slight increase in magnetization is attended with a large increase of volume. As the rate of increase appears to be nearly constant it would be interesting if we could push the field-strength still farther, to see whether the volume-change ultimately attains an asymptotic value.

The changes of volume and of length are shown in the following tables :—

### Change of Volume.

Nickel (1).		Soft Iron (3).		Steel (5).		Wolfram Steel (8).	
H.	$\frac{\delta v}{v}$ .	H.	$\frac{\delta v}{v}$ .	H.	$\frac{\delta v}{v}$ .	H.	$\frac{\delta v}{v}$ .
13	$0.09 \times 10^{-7}$	8	$0.10 \times 10^{-7}$	7	$0.08 \times 10$	19	$0.30 \times 10^{-7}$
30	0.29	11	0.52	12	0.47	42	1.52
90	0.65	18	1.56	33	1.95	93	3.03
218	0.82	167	3.12	192	3.13	216	5.01
282	0.97	443	3.85	376	4.69	442	8.04
517	1.38	691	4.58	586	6.22	692	11.68
877	2.06	958	5.88	792	8.01	1001	16.68
1141	2.44	1115	7.18	1044	10.16	1117	18.96
1547	3.24	1342	9.47	1376	14.07	1296	22.75
1740	3.53	1563	11.45	1646	17.20	1704	28.82
2253	4.12	2089	14.68	2171	22.20	2153	32.62

### Kirchhoff's Constants $k'$ and $k''$ .

Starting from the formulas

$$\lambda = \frac{\delta l}{l} = \left\{ \frac{4\pi k^2}{3} \left( \frac{1+\theta}{1+2\theta} \right) + \frac{k-k'}{2(1+2\theta)} - \frac{k''}{2} \right\} \frac{H^2}{E},$$

and

$$\sigma = \frac{\delta v}{v} = \left\{ \pi k^2 + 3 \frac{(k-k')}{4} - \frac{k''}{4} \right\} \frac{H^2}{K(1+3\theta)},$$

which give the change of volume and of length of ferromagnetic ovoids in terms of Kirchhoff's constants  $k'$  and  $k''$ ,

## Change of Length.

Nickel (2).		Soft Iron (4).		Steel (6).		Wolfram Steel (8).	
H.	$\frac{\delta l}{l}$	H.	$\frac{\delta l}{l}$	H.	$\frac{\delta l}{l}$	H.	$\frac{\delta l}{l}$
4	$-141 \times 10^{-7}$	6	$25 \times 10^{-7}$	13	$3.1 \times 10^{-7}$	18	$4.1 \times 10^{-7}$
6	$-64.0$	15	$19.0$	19	$7.1$	25	$12.4$
10	$-118.2$	51	$31.6$	28	$15.1$	39	$21.7$
15	$-163.6$	127	$23.8$	54	$22.2$	62	$28.9$
33	$-217.5$	224	$3.1$	96	$23.1$	106	$32.1$
59	$-264.3$	354	$-17.7$	160	$17.8$	170	$32.3$
124	$-317.6$	575	$-52.6$	225	$8.2$	235	$31.7$
302	$-343.6$	698	$-62.6$	374	$-11.5$	349	$30.2$
561	$-353.8$	883	$-73.5$	589	$-36.0$	592	$23.1$
839	$-356.0$	1077	$-78.9$	844	$-49.2$	781	$18.7$
1145	$-360.0$	1180	$-82.2$	1061	$-55.5$	1052	$17.0$
1289	$-360.9$	1324	$-86.6$	1177	$-59.5$	1188	$15.4$
1483	$-362.2$	1447	$-89.9$	1361	$-64.5$	1345	$13.9$
1849	$-362.7$	1598	$-91.6$	1729	$-69.9$	1697	$12.4$
2322	$-365.3$	2180	$-102.0$	2172	$-78.1$	2255	$10.9$

338 Messrs. Nagaoka and Honda on Change of Volume and we obtain the following expression for these two constants :—

$$k' = \frac{p(1+2\theta) - q}{2(1+3\theta)},$$

and

$$k'' = \frac{3q-p}{2(1+3\theta)},$$

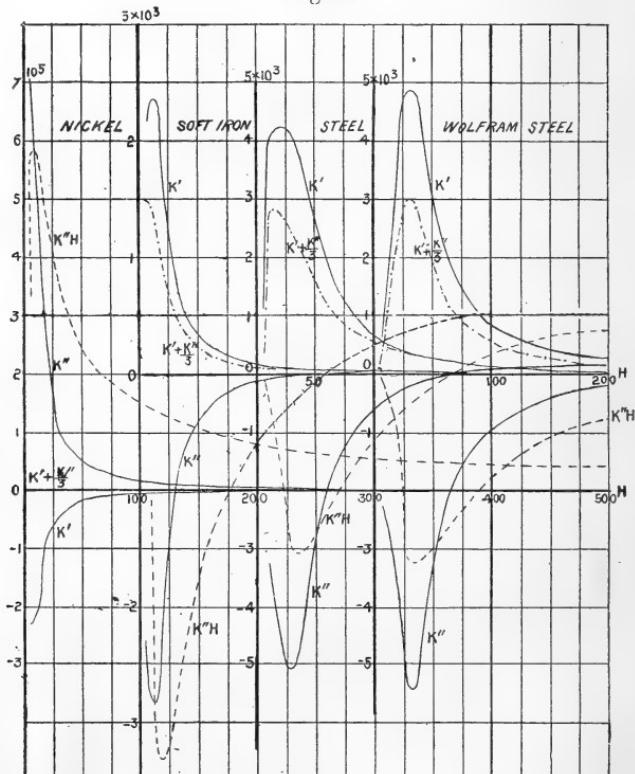
where

$$p = -\frac{4K(1+3\theta)}{H^2} \sigma + 4\pi k^2 + 3k,$$

$$q = -\frac{2E(1+2\theta)}{H^2} \lambda + \frac{8\pi k^2}{3} (1+\theta) + k.$$

These constants as calculated from the change of dimensions of ovoids are graphically shown in fig. 3.

Fig. 3.



The curves for  $k'$  and  $k''$  present the same general feature in iron, steel, and nickel. In iron and steel  $k'$  increases in low fields, reaches a maximum, and then rapidly diminishes till it becomes very small, so that the curve nearly coincides

with the axis of H.  $k''$  is at first negative, and attaining the minimum value goes on gradually increasing till it becomes greater than zero, and reaches a maximum of which the exact position is very vague ; ultimately the curve for  $k''$  coincides with that for  $k'$ . The position of the maximum for  $k'$  and that of the minimum for  $k''$  lies nearly in the same field, which is greater for wolfram steel than for soft iron, while that for ordinary steel occupies an intermediate position. The absolute values of  $k'$  and  $k''$  are greater in iron than in steel. In nickel, as already noticed, the values of  $k'$  and  $k''$  are far greater than those for iron and steel, and, moreover, are of opposite signs. The maximum of  $k''$  or the minimum of  $k'$  seems to lie in a weak field ; the rate of decrease or increase is quite rapid, and the curves for  $k'$  and  $k''$  soon approach the axis of H. Compared with the results of our former experiments, the absolute values of  $k'$  and  $k''$  are generally small for iron, but far greater for nickel. This difference arises from the fact that for iron the change of length in weak fields is less in this case than in the former experiment, and for nickel the contrary is the case. As regards the sign, these two experiments show fair agreement.

#### *Consequences of the Theory.*

*Effect of Longitudinal Pull.*—The change of magnetization produced by the elongation  $\lambda$  of the wire can be easily calculated from the formula

$$\delta I = H \left\{ k' \frac{E}{K} - 3 \left( k' + \frac{k''}{3} \right) \right\} \lambda.$$

Putting  $\lambda = 4.67 \times 10^{-6}, 4.80 \times 10^{-6}, 4.85 \times 10^{-6}, 4.74 \times 10^{-6}$  for soft iron, ordinary steel, wolfram steel, and nickel respectively, corresponding to a pull of 0.1 kilog. per sq. mm., we obtain the following results :—

H.	Soft Iron. $\delta I.$	Steel. $\delta I.$	Wolfram Steel. $\delta I.$	Nickel. $\delta I.$
10 .....	0.92	0.06	0.04	-24.6
20 .....	1.07	0.21	0.17	-18.9
30 .....	0.83	0.40	0.35	-14.2
60 .....	0.40	0.25	0.29	-9.1
80 .....	0.24	0.15	0.25	-7.1
100 .....	0.13	0.07	0.19	-6.0
120 .....	0.04	0.01	0.15	-5.2
160 .....	-0.08	-0.09	0.09	-2.7
200 .....	-0.16	-0.15	0.06	..
300 .....	-0.26	-0.21	0.02	-2.3
500 .....	-0.31	-0.24	0.00	-1.4
800 .....	-0.28	-0.20	-0.04	-0.9
1200 .....	-0.22	-0.16	-0.04	-0.6
1600 .....	-0.18	-0.13	-0.03	-0.5

It will be seen from the above table that in iron and steel there is increase of magnetization in low fields till it reaches a maximum, after which it gradually decreases. The decrease does not take place continuously, but reaches a maximum, whence the magnetization begins to recover. Although the former result here arrived at is the well-known Villari effect, we do not know whether the maximum decrease due to longitudinal stress has as yet been experimentally ascertained.

There is nothing remarkable in nickel. Longitudinal pull produces decrease of magnetization, which becomes gradually less as the field-strength is increased. This fact is so well-established by experiment that we need not enter into further discussion of the subject.

*Effect of Hydrostatic Pressure.*—We can easily see that the change of magnetization  $\delta I$  due to decrease of volume  $-\sigma$  by hydrostatic pressure is given by

$$\delta I = - \left( k' + \frac{k''}{3} \right) H\sigma.$$

As  $k' + \frac{k''}{3}$  is very small in nickel, the effect of hydrostatic pressure is very small compared to that of longitudinal pull. (See fig. 3, dotted-line.) There is increase of magnetization with the volume-contraction of the magnet. Such an increase reaches a maximum in a low field, whence the effect gradually diminishes. Similar changes are also to be noticed in iron and steel, quite contrary to experiment. The agreement between theory and experiment is very close in nickel, while there is wide discrepancy in iron and steel.

*Effect of Torsion on Longitudinally or Circularly Magnetized Wire.*—There are other important consequences to be drawn from the constant  $k''$  with regard to the effect of torsion on longitudinally magnetized wire and on ferromagnetic wire traversed by electric currents. The strain caused by twisting a circular wire can be resolved in elongation and contraction in directions perpendicular to each other and inclined to the axis of the wire at  $45^\circ$ . Taking these two principal axes of strain for those of  $x$  and  $y$ , we obtain the following expressions for the strains :

$$\frac{\partial u}{\partial x} = \frac{1}{2}\omega r, \quad \frac{\partial v}{\partial y} = -\frac{1}{2}\omega r, \quad \frac{\partial w}{\partial z} = 0,$$

where  $\omega$  denotes the amount of torsion and  $r$  the distance from

the axis. Thus

$$\delta I_x = -\frac{k''}{2} \omega r \frac{H}{\sqrt{2}},$$

$$\delta I_y = \frac{k''}{2} \omega r \frac{H}{\sqrt{2}},$$

$$\delta I_z = 0.$$

Consequently the circular magnetization which will be called into play is equal to  $-\frac{1}{2}\omega r \cdot k'' H$  at distance  $r$  from the axis, the mean circular magnetization being  $-\omega R k'' H$ , where  $R$  denotes the radius of the wire. The transient current which will be induced in the wire by suddenly twisting it, is proportional to  $k'' H$ .

Next suppose that the wire is traversed by an electric current of intensity  $C$ ; then the circular magnetizing force at distance  $r$  from the axis is

$$H = \frac{2Cr}{R^2}.$$

By applying similar reasoning, we find that the mean longitudinal magnetization is equal to  $-\omega k'' C$ . We therefore conclude that twisting the circularly magnetized wire gives rise to longitudinal magnetization proportional to  $k'' C$ . Thus the circular magnetization produced by twisting a longitudinally magnetized wire has reciprocal relation to the longitudinal magnetization caused by twisting a circularly magnetized wire\*.

The view put forward by Prof. Ewing † for explaining the existence of the transient current by means of æolotropic susceptibility is similar to what would follow from Kirchhoff's theory, but it fails to give the amount of the current or the magnetization which would be produced by twisting.

The theoretical inferences which we can draw at a glance from the curves of  $k'' H$  (fig. 3, dotted line) are as follows:—

1. The transient current as well as the longitudinal magnetization produced by twisting an iron or steel wire is opposite to that of nickel up to moderate fields.

2. The transient current as well as longitudinal magnetization produced by twisting an iron, steel, or nickel wire reaches a maximum in low fields.

3. In strong fields the direction of the current as well as

\* Voigt, *Compendium der theoretischen Physik*, Bd. ii. p. 203 (1896); Drude, *Wied. Ann.*, Bd. lxiii, p. 8 (1897).

† Ewing, Proc. Roy. Soc. vol. xxxvi. (1884).

the longitudinal magnetization is the same in iron, steel, and nickel.

It has been established by G. Wiedemann \* that the longitudinal magnetization produced by twisting iron wire traversed by an electric current is opposite to that in nickel. The opposite character of the transient current in these two metals has also been observed by Zehnder †, and independently by one of us ‡. The existence of a maximum transient current in these two metals has also been clearly established by the latter, although there is some difference in the field-strength between iron and nickel. It appears from the experiments of Dr. Knott § that the area of the hysteresis-curve in the longitudinal magnetization produced by twisting circularly magnetized wire reaches a maximum as the field-strength is increased; but on account of the feebleness of the current, the existence of the maximum in the longitudinal magnetization is not well established. Judging from the course of the curve given by the same experimenter, it seems highly probable that the maximum would be reached if we could push the circularly magnetizing force a little further. The conclusion (3) is still an open question, although some experiments of Matteucci || seem to corroborate the view above stated.

Looking at the curves of  $k''H$  (fig. 3), we are struck with the close resemblance of the curves representing the amount of torsion produced by the combined action of the circular and longitudinal magnetizing forces on a ferromagnetic wire. We can no doubt coordinate the effect of torsion on a magnetized wire with the Wiedemann effect. The discussion of the last-mentioned effect we hope to publish in the near future.

In spite of the qualitative explanations which Kirchhoff's theory affords with regard to the effect of longitudinal pull, of hydrostatic pressure in nickel, and of torsion, there are instances in which the theory apparently fails in several quantitative details, so that it necessarily calls for modification. We may remark that  $k'$  and  $k''$  are physically functions of the strain, as borne out by the numerous experiments on the effect of stress on magnetization. The present state of the theory of magnetostriction may perhaps be compared with that stage in the history of the theory of magnetism when the

\* G. Wiedemann, *Elektricität*, Bd. iii.

† Zehnder, Wied. Ann. Bd. xxxviii. p. 68 (1889).

‡ Nagaoka, Phil. Mag. vol. xxix. p. 123 (1890); Journal of the College of Science, Tōkyō, vol. iii. p. 335 (1890).

§ Knott, Trans. Roy. Soc. Edinb. vol. xxxvi. p. 485 (1891).

|| Matteucci, *Annales de Chimie et de Physique*, 1858.

intensity of magnetization was supposed to be simply proportional to the magnetizing force. In fact, the theory is still in its infancy, so that there are ample grounds for further development and research.

Physical Laboratory, University of Tōkyō,  
December 20th, 1899.

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**XXXI. Some Developments in the Use of Price's Guard-Wire in Insulation Tests.** By Prof. W. E. AYRTON, F.R.S., and T. MATHER \*.

EVERYONE who has to test very high resistances, such as those of short lengths of cable and of good joints in insulated wires, cannot fail to appreciate the immense advantage of using Price's "Guard-Wire" † in eliminating errors due to surface leakages. Continued experience confirms the opinion expressed by one of us in the discussion on Mr. Appleyard's paper in 1896; and in our third paper on Galvanometers, read before the Physical Society in May 1898 ‡, we showed how the principle could be applied to galvanometers, shunt-boxes, &c.

For tests made by the "direct deflexion" method the "guard-wire" properly applied affords complete protection against surface leakage where the ends of the cable tested are near the galvanometer, so that it is possible to have the wire connecting the conductor of the cable with the galvanometer terminal "air insulated." A difficulty, however, arises when the ends of the cable are at a considerable distance from the testing instrument; this may render "air insulation" of the lead impossible, and so the leakage from the lead must be measured and allowed for. As this "lead leakage" may be as large as or larger than that through the mass of the insulation under test, the convenience and accuracy of the measurement are somewhat impaired. It therefore occurred to us that a guard-wire applied to the lead along its entire length would prove of great value in cases such as the one under consideration. The most effective as well as the simplest way of doing this is to use a concentric wire to connect the cable and galvanometer, the inner of the

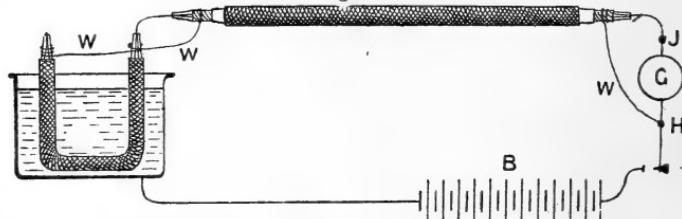
\* Communicated by the Physical Society: read January 26, 1900.

† Electrical Review, vol. xxxvii. p. 702 (1895). See also Appleyard on "Dielectrics," Phil. Mag. xlvi. p. 148 (1896); Proc. Phys. Soc. vol. xiv. pp. 257, 264.

‡ See Phil. Mag. Oct. 1898, p. 368, and Proc. Phys. Soc. vol. xvi. p. 191.

concentric being used as the "lead," and the outer as the "guard-wire."

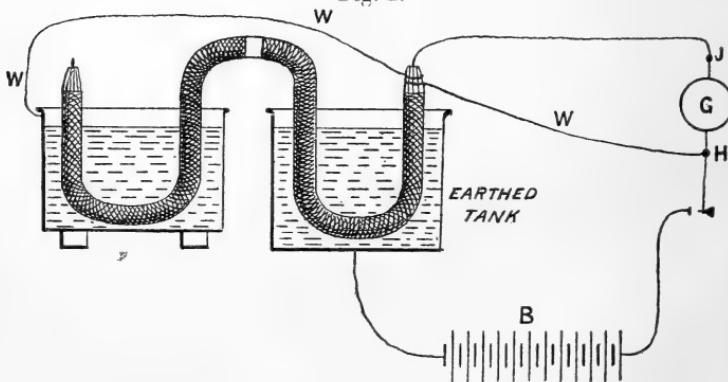
Fig. 1.



The arrangement is shown symbolically in the sketch above. It will be readily understood that so long as the insulation resistance of the outer of the concentric is high compared with the internal resistance of the battery the method indicated gives complete protection against lead leakage and surface leakage, even if the concentric be laid along the ground for a considerable distance.

Other instances in which special applications of the guard-wire principle have been found convenient have arisen in cases where it has been necessary to determine whether a defective piece of cable was bad throughout, or bad owing to one or more isolated faults. When two tanks are available and one of them can be moderately well insulated from earth, the method of procedure is to coil about half the cable in each tank, remove the metal sheathing (if any) from a short length, say one inch, of the cable between the two tanks, and connect the guard-wire with the insulated tank as well as

Fig. 2.



wrap it round the insulating covering near the extremity of the cable as shown in fig. 2. In the case of braided and other unsheathed cables, the covering of the portion between

the two tanks need not be removed. An insulation test applied under the above conditions gives the resistance of the part of the cable in the earthed tank, and a comparison of this with the insulation resistance of the whole will show whether one half is worse than the other half. By repeating this test with say one quarter of the cable in the earthed tank, and the remainder in the other tank, the question of local *v.* general leakage may be decided.

Instead of two tanks, two drums, one of which can be fairly well insulated, might be employed, or one drum and one tank used, for we find that after the braiding of a cable has been thoroughly wetted it acts as a fair conductor for several hours, even on a dry day. It is therefore not essential to have the part tested completely immersed, although of course immersion is conducive to constancy of temperature. Sufficient connexion with the wet braiding can be made by wrapping bare wire round it. If the cable be long this may be done at several places along its length.

By employing the two drums above mentioned faults in braided and other unsheathed cables can be readily localized, without in any way injuring the cable. After connecting the guard-wire with the insulated drum the wetted cable is wound from the earthed drum to the insulated one, the galvanometer being connected with the inner conductor during the process. When the fault passes to the insulated drum a sudden diminution of deflexion occurs.

In some cases we have only used one tank (the earthed one in fig. 2) in testing part of a coil of cable, the remainder being first wetted and hung up on a wooden beam supported between two tables. By inserting metal sheets connected with the guard-wire between the beam and the tables errors which might otherwise arise from surface leakage are eliminated.

The guard-wire properly applied gives complete protection against surface-leakage errors when the tests are made by the "direct deflexion" method, but in the "loss of charge" test it is desirable to make measurements both with and without a guard-wire. Unless this be done one cannot be sure that surface leakage is not influencing the results obtained.

A little consideration will show that if any surface leakage exists a guard-wire will tend to keep up the potential of the inner conductor during the period of "insulation," and therefore cause the insulation resistance to appear *greater* than its true value; whereas if no guard-wire be used surface leakage will facilitate discharge and cause the insulation resistance to

appear *less* than its true value. If, however, the two tests give about the same result (care having been taken to properly discharge the cable between them) we have proof that the effect of surface leakage is inappreciable. It is frequently more expeditious to make the two tests above mentioned than to clean and coat the ends with paraffin-wax in such a way as to make one feel confident that no surface leakage exists.

In making the guard-wire measurements it is desirable to put the guard as near the braiding or sheathing as practicable, consistent with keeping the resistance between the guard-wire and the sheathing high compared with that of the battery. By so doing any error due to the guard-wire is lessened, for the path over which surface leakage can occur is made as long as possible and nearly equal to that over which leakage takes place when no guard-wire is used. An approximate correction is then possible, even when the two tests with and without the guard-wire do not give the same result.

Suppose, for example, the swing of the galvanometer-needle on the first charge is  $s_1$  divisions, and  $s_2$ ,  $s_3$  were the swings on "recharge" after the same period of "insulation" with and without guard-wire respectively, then the value of the recharge swing, if no surface leakage existed, would be given by the expression

$$s = \frac{s_2}{1 - \frac{s_3 - s_2}{2s_1}} \text{ approximately.}$$

The preceding formula is generally sufficiently accurate for practical purposes, but it is possible to obtain *absolute* accuracy in the use of the guard-wire with the "loss of charge" insulation test in the following way. Instead of maintaining the potential of the guard-wire constant, while that of the insulated conductor is steadily falling, cause the potential of the guard-wire to fall at the same rate as that of the insulated conductor. Then no electricity can pass between the conductor and the guard-wire, and surface leakage will be absolutely prevented.

A potentiometer and an electrostatic voltmeter can be conveniently employed in carrying out this experiment, and it is interesting to remember that the Thomson and Varley potentiometer was originally devised for the special object of enabling the potential of one conductor to be made to diminish as the potential of another conductor steadily fell

by leakage. This was not of course in connexion with the use of Price's ingenious guard-wire, but in the days of the old "divided-ring electrometer," before it was known how to make a quadrant electrometer with the deflexions *directly* proportional to the P.D. to be observed, and when, therefore, a zero method had to be employed in carrying out the "loss of charge" insulation test.

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*XXXII. The Frequency of Transverse Vibrations of a Stretched Indiarubber Cord.* By T. J. BAKER, B.Sc.\*

THE writer has observed that the pitch of the note produced by twanging an indiarubber band which is stretched over the fingers is influenced but little by the tension, particularly if this is considerable.

The matter appeared worthy of further investigation; and for this purpose a short piece of indiarubber cord, of square section, was attached at one end to the middle of a tambourine-diaphragm, while the other end was bound to a piece of twine which passed over a pulley-wheel and supported a weighed scale-pan.

After placing a weight in the pan, the rubber was allowed to stretch for some minutes, and then the end nearest the pan was firmly clamped. The intensity of the note produced by transverse vibrations of the cord was rendered sufficiently great by the tambourine to permit a determination of pitch by comparison with a sonometer and tuning-fork.

The sectional area of the cord under the various tensions employed was determined by measurements of its two diameters at three different points in its length.

For this purpose a micrometer-gauge reading to .001 cm. was employed. The observations were continued until the cord broke. This happened when its length had increased six-fold. The 38 sets of values thus obtained were plotted on squared paper, and three curves were drawn showing the relation between—

- (i.) Length and tension.
- (ii.) Length and sectional area.
- (iii.) Length and frequency.

The smoothing-out of slight experimental irregularities

\* Communicated by the Physical Society: read Jan. 26th, 1900.

which these curves effect was found of advantage in the calculations hereafter referred to.

Inspection of the curve connecting length with tension reveals that the relation is strictly linear between those points at which the length of the cord becomes respectively  $2\frac{1}{2}$  and 5 times its natural length.

Untrustworthy readings were obtained with further stretching because an increase of tension did not produce its full effect until a very considerable time had elapsed. With the smaller stretchings this difficulty was not encountered.

The curve connecting length with frequency shows that while the cord was doubling its natural length the pitch of its note was rising rapidly; but that further extension was practically without effect.

When the cord had doubled its natural length, its frequency of vibration was 91; and when its original length had been sextupled the frequency was not more than 94.

The discussion which follows relates to the conditions prevailing during the period in which length and tension are connected linearly.

Since the observations show that equal increments of tension (between the limits above mentioned) produce equal extensions; and at the same time the sectional area is diminishing, it appears that the value of Young's modulus must increase with increasing extension.

Experiments have been made on this point by Villari (*Pogg. Ann. cxliii.*), by Röntgen (*ibid. clix.*), and by Mallock (*Proc. Roy. Soc. 1889*); but beyond ascertaining that Young's modulus increases rapidly with increase of extension no definite relations appear to have been discovered.

The values of the modulus for the cord used in these experiments were therefore calculated by the use of curves (i.) and (ii.).

In each case an extension of 1 cm. was chosen, and the increase of tension required to produce this was 16 grams weight.

The mean value of the sectional areas before and after each increase of tension was used in the calculation; and for this purpose curve (iii.) was employed.

When the results are tabulated, it becomes apparent that *Young's modulus is proportional to the square of the stretched length of the cord.*

The last column in the table exhibits this relation.

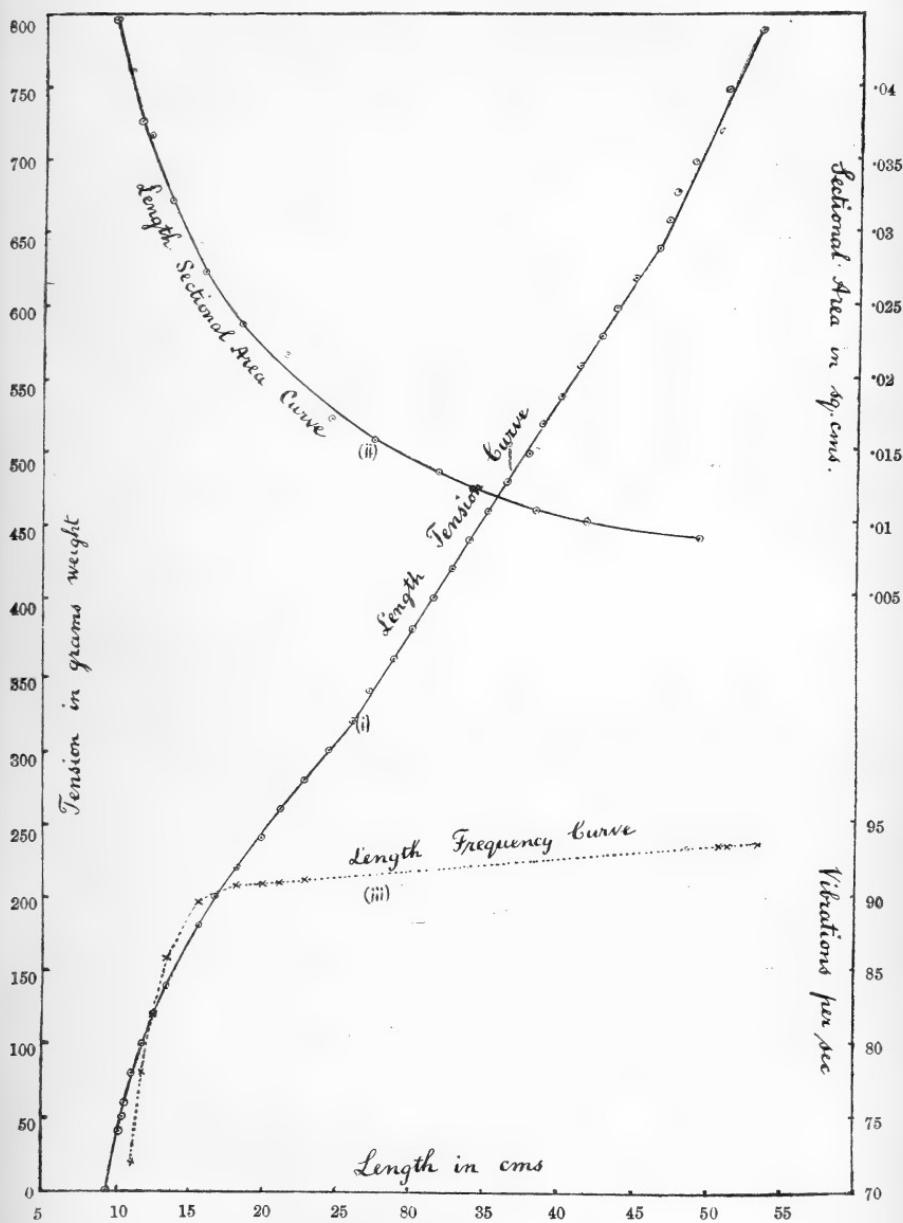


TABLE showing Relation between the stretched Length of an Indianrubber Cord and the corresponding Value of Young's Modulus.

Natural dimensions of the cord 9·3 cm.  $\times$  22 cm.  $\times$  221 cm.  
Frequency of the stretched cord = 93.

Original Length in cms.	Final Length in cms. (L).	Sectional Area in sq. cms.	Increment of Tension in grams weight.	Young's Modulus (Y).	$\frac{Y}{L^2}$ .
26 .....	27	.0159	16	26163	35·9
28 .....	29	.0148	16	30270	36·0
30 .....	31	.0138	16	34782	36·2
32 .....	33	.0128	16	40000	36·7
34 .....	35	.0121	16	44958	36·7
36 .....	37	.0112	16	51200	37·3
38 .....	39	.01057	16	57508	37·8
40 .....	41	.0101	16	63366	37·6
42 .....	43	.0097	16	69278	37·4
44 .....	45	.0094	16	74734	36·9
45 .....	46	.00927	16	78431	37·0

If this relation is borne in mind, it can be shown that the frequency of a greatly stretched rubber cord will increase very slowly indeed with increase of tension.

Let  $T$  = tension.

$l$  = natural length of the cord.

$L$  = stretched

$m$  = mass of unit length of cord.

$w$  = mass of cord.

$\rho$  = density of the rubber.

$s$  = sectional area of the cord.

$Y$  = Young's modulus.

Then between the limits previously specified,

$$\frac{dT}{s} = Y \frac{dL}{L}.$$

But

$$\rho s L = w;$$

$$\therefore \rho \frac{dT}{w} = Y \frac{dL}{L^2}.$$

Now since it has been shown that

$$Y = kL^2;$$

$$\therefore \rho \frac{dT}{w} = k.dL;$$

$$\therefore \frac{\rho}{w} T = kL + C*.$$

\* This assumes  $\rho$  constant. Villari found the density of rubber which was stretched four times its natural length to be .966 times its natural density.

Put  $T=0$  when  $L=l$ ,

$$\frac{\rho}{w} T = k(L-l).$$

But

$$\begin{aligned} w &= Lm, \\ \therefore \frac{\rho T}{Lm} &= k(L-l); \end{aligned}$$

and

$$\frac{1}{L^2} \cdot \frac{T}{m} = \frac{k}{\rho} \left( \frac{L-l}{L} \right).$$

Also for a vibrating string

$$\begin{aligned} n &= \frac{1}{2L} \sqrt{\frac{T}{m}}; \\ \therefore n &\propto \sqrt{\frac{L-l}{L}}. \end{aligned}$$

The value of this expression increases very slowly with increase of  $L$  if the latter is several times  $l$ . This appears to be the explanation of the remarkable constancy in pitch of the note given by the vibration of a rubber cord under increasing tension\*.

King Edward's School, Birmingham.

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XXXIII. *On the Controversy concerning Volta's Contact Force.* By Professor OLIVER LODGE, D.Sc., LL.D., F.R.S.†

## CHAPTER I.

### *Thermodynamic Arguments.*

THOSE who take what I may call a metallic view of the Volta contact-force are accustomed to deny that the Peltier evolution of heat measures the local E.M.F. existing at a junction ; they assert instead that it measures the rate at which that same E.M.F. varies with temperature :—

$$\Pi = T \frac{dE}{dT}.$$

Let us examine this assertion.

\* Since this was written, the author's attention has been directed to a paper on the same subject by von Lang (Wied. *Ann.* vol. lxviii.). The constancy of pitch is briefly mentioned as due to an observed proportionality between the tension and the stretched length of the rubber cord. The paper deals chiefly with small discrepancies between the frequencies observed and those calculated from Taylor's formula.

† Communicated by the Physical Society, being the Presidential Address for 1900.

An equation of this general shape is undoubtedly true, but it has not the meaning which they assign to it.

The  $\Pi$  may refer to a particular junction, and in certain cases does, but the  $E$  does not. The  $E$  means the total E.M.F. of the complete circuit, always.

I venture to think that this will not be disputed, if the matter be for a few moments carefully attended to. To assist attention we may go carefully over some elementary ground—so elementary that it is difficult to secure for it that amount of attention which is necessary for clearness.

The thermoelectric power of a metal A at various temperatures means the function which is plotted in an ordinary thermoelectric diagram, with temperatures as abscissæ, relatively to some standard metal (lead) taken as the line of reference or constant zero of thermoelectric power.

To determine this function a circuit has to be constructed with the metal A and the standard metal O, their junctions brought to different and known temperatures  $t$  and  $t'$ , and the resulting E.M.F. (the whole E.M.F. of the circuit) observed, being measured either by the strength of current developed, or better, by a potentiometer or compensation method. Then the ratio  $E/(t'-t)$  is called the thermoelectric power of the metal A at the mean temperature  $\frac{1}{2}(t+t')$ , and is plotted accordingly, for a considerable range; the differences  $t'-t$  being naturally kept small, in case the resulting function is not linear.

This is done likewise for other metals, B, &c.; and the relative thermoelectric power of two metals at the same temperature (being  $P_{AB} = P_B - P_A$ ) is represented by the vertical distance between the A and B lines of the diagram.

Another function of temperature is likewise represented in the diagram, not by a length but by a rectangular area, bounded on the right by the thermoelectric height, and on the left by the line of absolute zero. This is the function  $\Pi$ , such that

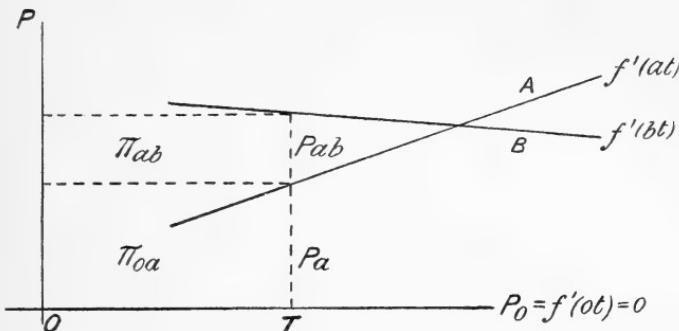
$$\Pi_{OA} = P_A T, \text{ and } \Pi_{AB} = P_{AB} T.$$

It is to be observed that in this diagram (apart from the experimental mode of obtaining real values for  $P$ ) no reference is so far made to any junctions, nor to any circuit, nor current, nor E.M.F., nor evolution of heat; it represents nothing but a geometrical plotting of certain metallic properties as functions of absolute temperature.

If we now connect the two metals at one point, they are necessarily at the same temperature, say  $T_1$ , at that point;

their relative thermoelectric power at the junction,  $P_{ABT}$ , may be called  $\Pi_1$ ; and the area just spoken of is  $\Pi_1 = P_1 T_1$ .

Fig. 1.



Now Lord Kelvin showed in 1856 that this  $\Pi_1$  is the Peltier coefficient, *i.e.* that it measures the reversible heat generated at the junction if a unit quantity of electricity is transmitted across it.

If we proceed to connect the two metals also at some other point, at some other temperature  $T_2$ , there will of course be an appropriate value for  $P_2$  and  $\Pi_2$ , but there is more than that: every intermediate point of one metal will have a temperature corresponding to that at some intermediate point of the other metal, and accordingly there is a  $P$  and a  $\Pi$  appropriate to every intermediate temperature.

There will also be now a closed circuit, and a current, driven by a resultant electromotive force, which may be expressed instructively in the following different ways,

$$E_{AB} = \text{cycle} \int P dt = \int_1^2 P_{AB} dt = \int_1^2 \Pi d \log T = f(t_2) - f(t_1);$$

the function  $f$  being such that

$$\Pi_{AB} = T f'(t) = T \frac{d}{dt} E_{AB} \text{ everywhere.}$$

At the junctions there is now a reversible generation of heat per second

$$\Pi_1 = T_1 f'(t_1) \quad \text{and} \quad \Pi_2 = T_2 f'(t_2)$$

per unit current.

In the metals there is likewise a reversible generation of heat

$$\Theta_a = \int_1^2 \sigma_a dt, \quad \Theta_b = \int_1^2 \sigma_b dt,$$

such that

$$\sigma_a - \sigma_b = T \frac{d^2 E}{dT^2} = T f''(t);$$

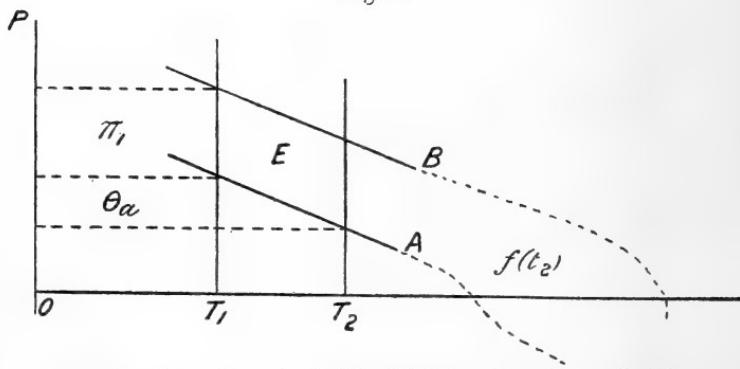
and the total E.M.F., in addition to the modes of writing adopted above, may also be represented as,

$$E = J(\Pi_1 - \Pi_2 + \Theta_a - \Theta_b),$$

since  $E$  represents the work done per unit quantity of electricity conveyed.

The representation of all this in a thermoelectric diagram is neat and convenient, and is sufficiently shown in the figure, without overlapping of areas.

Fig. 2.



Remembering that it is  $P$  which is plotted vertically, and that  $P = \Pi/T$  everywhere, the whole of the above various expressions for the area  $E$  are geometrically represented. The only one needing explanation is the expression  $f(t_1) - f(t_2)$ , the difference of two indefinite-integral areas, of which the second limit is incomplete in the figure, because unknown. All that is known about  $f'(t)$  is that  $E$  is the difference between its values at the temperatures  $t_1$  and  $t_2$ , that  $f'(t) = \Pi_{AB}/T$  everywhere, and that  $f''(t) = (\sigma_a - \sigma_b)/T$  everywhere. But the value of the function  $f'(t)$  itself is not known; nor is there any means of determining it from observed values of a current in a closed thermoelectric circuit. (I have no reason for depicting this area in the diagram on the right towards infinity, instead of on the left towards absolute zero, except that thereby overlap is avoided. Otherwise one would naturally draw it so as to be bounded hypothetically by the line of absolute zero. The diagram does not attempt to represent its probable value, but merely to emphasize the fact that its absolute value is not known or needed in ordinary thermoelectricity.)

Excepting in portions relating to  $f(t)$  there is, I apprehend, so far no controversy. And yet, if all this be admitted, my contention that, in the equation  $\Pi = TdE/dt$ , the E refers to the whole circuit and not to any particular part of it, though the  $\Pi$  may refer to a junction, is substantiated.

Nevertheless this statement has been, and probably still will be, seriously disputed \*, but I hope that if it is still disputed the actual subject will be dealt with, and not hydraulic illustrations of doubtful applicability given.

Controversy begins as soon as localization is attempted ; as soon as one says that  $J\Pi_1$  is a measure of the E.M.F.

\* For instance, I might quote several physicists who have said (somewhat casually, as I think), since a discussion at the Institute of Electrical Engineers (Journ. Inst. E. E. 1885), that the Peltier heat-evolution is no measure of a contact E.M.F. existing at the junction where it occurs, but is a measure of the rate of variation of this E.M.F. with temperature ; but it will suffice if I quote part of Prof. Ayrton's remark in that same discussion, with an occasional interposition of my own in square brackets, because he expresses himself clearly and strongly—always a desirable thing to do :—

"Dr. Lodge's fundamental argument—the argument in fact upon which his whole paper is based—is this: He *assumes* that in all cases where there is a considerable difference of potential at a [metallic] junction, heat or cold must be developed when a current flows across that junction." [I should myself word it rather differently, to avoid misunderstanding, though misunderstanding is hardly possible in what follows ; but apart from possible misunderstanding I have no objection to the statement, except that I do not regard it as an *assumption*, unless the conservation of energy is an assumption.] "He states what is quite true and well known—that practically no heat is developed when a current flows from zinc to copper across the junction; therefore he concludes that there can be no contact-potential difference at this junction like three-quarters of a volt. But this reasoning is based on a totally wrong conception of the Peltier effect, which I am astonished to find exists in the mind of a man with the scientific powers of Dr. Lodge. *The amount of heat generated when a unit current is sent through a junction for a second is undoubtedly the measure of the coefficient of the Peltier effect; but this coefficient is in no sense a measure of the contact-potential difference existing at the junction.*" [Italics are Prof. Ayrton's.] "What the Peltier effect, at a junction of the two substances at a given temperature, measures, is the product of the absolute temperature into the rate of variation, with temperature, of the contact-potential difference at that temperature; in other words, if  $\Pi$  is the Peltier effect at a junction which is at an absolute temperature  $t$ , and if  $V$  is the contact-potential difference at that temperature,  $\Pi = t \frac{dV}{dt}$ .

"Hence the magnitude of  $\Pi$  does not measure  $V$ , but merely  $t \frac{dV}{dt}$ , and the error of Dr. Lodge is of the same sort of order as saying that a train going at a very nearly uniform speed is necessarily moving very slowly because the change of speed per second is very small. This disposes of the objection based on the smallness of the Peltier effect." [No, it is not disposed of quite so easily as that. The difference between velocity and acceleration is somewhat familiar.]

existing at the junction whose temperature is  $T_1$ , and that  $J\Theta_a$  is a measure of the E.M.F. existing along the gradient of temperature in the metal A.

Controversy also begins in respect of the function  $f(t)$ \*. There are those who decline to take an agnostic position with respect to the absolute value, or second limit, of this function, and who say that it represents absolutely the Volta contact force ; that is, the E.M.F. observed in the dielectric space between two metals when a metallic circuit is not completed, when there is only one metallic junction, and when a dielectric space is substituted for the other junction. The value of the E.M.F. thus observed is very large, say a thousand times as big as any we have been so far dealing with ; it is not observable in any closed metallic circuit, it is only observable in a dielectric portion of a circuit, and it has no apparent connexion with thermoelectricity ; hence, those who assert that this great E.M.F. is represented by  $f(t)$ , that is, by a function of the metallic junctions otherwise and solely known by its differences and derivatives in thermoelectricity, should be prepared with a definite proof of their statement. So far as I know a proof has never even been attempted. To me it appears that the introduction of a dielectric or an electrolyte into the circuit, with its necessary two new junctions, each with chemical potentiality, has entirely altered the whole conditions ; and that no longer can it be said that the above laws, appropriate to a closed metallic circuit, apply. I maintain that whether the assumption, that  $f(t)$ , a function of the metallic junctions alone, represents the Volta effect observed in the air when a circuit is broken, is made tacitly or explicitly it is made gratuitously and requires justification, which, so far as I know, has not yet been forthcoming.

To show that the unsupported statement just referred to—whereby the Volta effect, a potential gradient observed in the air when a metallic circuit is broken, is introduced into a thermoelectric function of metals alone, with which it appears to me to have nothing to do—is responsibly made, I might quote from several writers ; but there is no need to quote more than Lord Kelvin's statements in his Friday evening discourse to the Royal Institution for May 1897 (Reprinted in the Phil. Mag. July 1898) :—

“ § 19. Seebeck's great discovery of thermoelectricity (1821) was a very important illustration and extension of the twenty years' earlier discovery of the contact-electricity of dry metals by Volta. It proved independently of all dis-

\* Cf. Phil. Mag. March 1886, p. 267.

turbing conditions that the difference of potentials between two metals in contact varies with the temperature of the junction." [This is no doubt true as it stands, if the junction is the only part heated ; the Seebeck force is superposed upon the Volta force, and hence the electrostatic effect observable in an incomplete circuit is naturally slightly affected by differences of temperature, though not necessarily by absolute uniform temperature. The break of circuit may be made in the middle of one of the metals whose junctions are maintained at different temperatures, in which case only the Seebeck force could possibly be electrostatically observed (that is, a combination of Peltier and Thomson effects) by a sufficiently sensitive electrometer ; or the break may be made between the two metals, in which case the much greater Volta force will be observed in the air-gap in combination with the insignificant Peltier force of the metallic junction ; and any fluctuation of temperature to which that remaining metallic junction is subjected will but vary this insignificant superposition upon the true Volta effect. But the sentence quoted is not intended to convey this meaning ; what it is intended to convey is that the Volta gradient of potential observed in the gap is chiefly due to something occurring at the remaining metallic junction, and that this something is a function of the temperature. Indeed, a later sentence (§ 26) clearly states, not only the existence of this large metallic-junction force, but also its cause.] "This force" [viz. the force of attraction between the oppositely-charged metals across a gap], "properly viewed, is a resultant of chemical affinity between thin surface-layers of the two metals."

[And then the author goes on to explain that the junction-force at the boundary of two metals has nothing whatever to do with any reversible heat-effects which may be observed there ; because, if it had, these reversible heat-effects would be vastly larger than in fact they are. It is therefore argued that these Peltier effects by no means represent the value of the E.M.F. existing at the junction where they occur, but represent only the rate at which this E.M.F. varies with temperature,  $\Pi = TdE/dT$  ; whereas, as I have said above, the E really appropriate to this equation is not located at the junction at all, but is the resultant or integrated E.M.F. of the whole circuit. However, I continue the quotations, not at first using quotation marks simply because the wording is abbreviated where no precision is required.]

Imagine a circuit of two metals—say iron and copper ; and

let the copper be cut across in the middle, so that an independent E.M.F. can be introduced by wire electrodes and a current maintained across the two junctions. "The Peltier heat produced where the current passes from iron to copper is manifestly not the thermal equivalent of the work done." [This sentence is ambiguous. It may mean the "work done" on the *whole circuit*, in which case it is true; it may mean the "work done" precisely *at the junction*, in which case I should say that the word "not" ought to be omitted. The immediate context suggests the former interpretation; the next succeeding context suggests the latter. The immediate context runs as follows.]

"In fact, if the two junctions be at equal temperatures, the amounts of Peltier heat produced and absorbed at the two junctions will be equal, and the work done by the independent E.M.F. will be spent solely in the frictional generation of heat." [This is undeniable, though not apparently to the point; but the next section continues]

"Many recent writers, overlooking . . . obvious principles, have assumed that the Peltier evolution of heat is the thermal equivalent of E.M.F. at the junction. And in consequence much confusion, in respect to Volta's contact-electricity and its relation to thermoelectric currents, has clouded the views of teachers and students. We find over and over again the statement that thermoelectric E.M.F. is very much smaller than the Volta contact E.M.F. of dry metals. The truth is, Volta E.M.F. is found between metals all of one temperature, and is reckoned in volts, or fractions of a volt, without reference to temperature." [Certainly.] "If it varies with temperature, its *variations* may be stated in fractions of a volt per degree." [By all means.] "On the other hand, thermoelectric E.M.F. depends essentially on *difference of temperature*" [the thermoelectric force of a complete metallic circuit does, and not the thermoelectric force at any particular junction; that depends on the temperature of the junction, and cannot be affected by the temperature somewhere else] "and is essentially to be reckoned *per degree*; as, for example, in fraction of a volt per degree." [Not so; an electromotive force of any kind whatever must be reckoned in volts. Volts per degree is not E.M.F., but is the so-called relative thermoelectric power of two metals.]

I have ventured thus to interpolate what I consider corrective remarks in brackets into this readily accessible quotation, because of a preceding sentence with which I quite agree, viz. this:—"Peltier's admirable discovery . . .

is highly important in theory, or attempts at theory, of the contact electricity of metals”\*.

\* To this I might add, what I now see more clearly than before, that it is more particularly the mode of statement of Lord Kelvin’s own “admirable discovery” that is really the central feature of this part of the controversy. For there are three, at least three, modes of regarding it :—

1st. A convection of heat pure and simple—electricity acting as a fluid with a positive or negative specific heat, and conveying heat down or up a temperature gradient.

2nd. An E.M.F. acting in metal from hot to cold or from cold to hot, and thereby either opposing or assisting the passage of a current, in the one case developing extra local heat, in the other case consuming heat or developing local cold, proportional to the local E.M.F. and the current.

And this 2nd mode has two subdivisions :—The E.M.F. thus supposed to exist from end to end of a metal bar with its ends at different temperatures, may display itself :—

either (a) as a gradient of potential in the air outside, detectable by an abnormally sensitive electrometer-needle, but never yet observed ;

or (b) as a change in the step of potential from metal to air, according to the temperature of the metal; the air-potential outside being left uniform.

But there is yet the third method of regarding the whole matter :—

3rd. As a mere modification of the junction E.M.F. with temperature, so that the Peltier function, which had been of the value  $kt(t_0 - t)$ , is modified by addition of a term  $\frac{1}{2}kt^2$ , so that it becomes  $kt(t_0 - \frac{1}{2}t)$ .

On this plan, no E.M.F. of any kind is supposed to exist in the single metal itself, no more than when its temperature was uniform, all the E.M.F. is thrown upon the junctions; the E.M.F. of the circuit is simply the difference of the junction-forces, as it would have been had there been no Thomson effect; but each junction-force, by reason of the Thomson effect, has somehow attained a quadratic term; their difference therefore permits thermoelectric reversals and the observed law of the thermoelectric circuit, for subtracting the two junction-forces we get

$$E = k(t_1 - t_2)(t_0 - \bar{t}).$$

This third mode is evidently the way in which several philosophers have been accustomed to regard the matter; and on the hypothesis that junction-forces in a metallic circuit are due to the affinity of metals for each other, it is natural to locate all the E.M.F. at the junction of two different metals, and to deny any E.M.F. between different parts of one and the same metal at different temperatures. (This is very different from the experimental fact that the resultant E.M.F. round a homogeneous metallic circuit is zero.) Those who regard the junction-forces as physical would naturally take a different view. For instance, take Helmholtz’s hypothesis of a specific attraction of metals for electricity, the same being a function of temperature: a differential attraction between the hot and cold ends of a bar would be just as essential as a differential attraction at the junction of metals of different kinds. It has been asserted that Helmholtz’s view tends to concentrate the force at the junctions and to make the Peltier heat proportional to the rate of variation of the local junction-force with temperature. But even if it does, and later we will show that it does not, no view makes this junction-force

And in case anything that I can say can make the matter clearer, I would reassert that since E.M.F. is work per unit charge conveyed, not only for the whole circuit but for any portion of a circuit, and since a unit charge conveyed across a junction develops an amount of heat  $\pm \Pi$ , it follows that the physical E.M.F. located at that junction is measured by and is equal to  $\mp J\Pi$  (assisting the current in one direction and thereby consuming heat or developing cold, opposing it in the other direction and therefore developing extra heat); unless some other mode of accounting for the appearance or non-appearance of the reversible heat is devised, or unless the reversible energy takes some other form than heat.

Wherever energy appears or disappears in a circuit, there, in that place, must be located an E.M.F. It may be, so to speak, the frictional E.M.F. appropriate to Ohm's law in a homogeneous conductor; it may be the chemical E.M.F. at a fluid or semifluid junction discovered by Volta; or it may be the contact-force at a solid junction, of which the integral round a whole circuit of non-uniform temperature was discovered by Seebeck, the locality of part of that E.M.F. by Peltier, and the locality and existence of the rest of that E.M.F. by Lord Kelvin.

At a chemical junction the reversible energy need not all of it or much of it take the form of heat, and in that case the major part of the E.M.F. may be rightly called chemical, not physical; but at a metallic junction, as in a homogeneous conductor, heat is usually the only form of energy expected or observed, and in that case wherever the E.M.F. is located there the heat or cold must appear. The ordinary way out of this conclusion is to suppose that electricity is a fluid with a real specific heat whose value changes from metal to metal, so that heat can be evolved or absorbed at a junction by a sudden change in the heat-capacity of the electric fluid flowing across

the same as the Volta effect, or suggests that the Volta effect has anything to do with the matter; except on the hypothesis that the air layer intervening when a metallic junction is broken is utterly inert and impotent.

It is no argument in favour of the impotence of the air layer to say that it produces no apparent effect when it bathes the metal uniformly all round; the question is what it does when uniformly all round does not exist. Balanced forces are not the same thing as no force, although they produce the same zero accelerative effect. Nor does the absence of acceleration prove the absence of all force. A body subject to balanced forces and obeying the first law of motion is a frequent spectacle—a railway train or a snowflake for instance—but a body subject to no forces is decidedly rare.

it, without the need for any local performance of work or any corresponding local E.M.F.\*

I should be glad to know whether any objectors to what I may call the Maxwellian view—the view of the precise local correspondence between E.M.F. and reversible heat-effects—do seriously base their opposition on this ground of a real physical specific heat of electricity. The only other alternative that I can see (short of Helmholtz's theory, to be mentioned later) is to say that the metallic junction is really a chemical junction too, that the energy does not take the form of heat because it takes that of chemical combination, and to point to a weighable quantity of alloy or other compound produced at that place by the passage of a current. Whether or not any chemical compounds are really formed at a given junction, then becomes a simple question of fact.

Since a voltaic circuit never has less than three junctions, and since we are trying to apply to it as much of the thermoelectric laws as it will stand, it may be well to write down these laws for the case of a metallic circuit with any number of metals, and therefore with a thermoelectric diagram having discontinuities at the several junctions,—everything discontinuous but temperature. Each metal, referred to the standard, has a certain thermoelectric power at each temperature, and accordingly the resultant E.M.F. of the circuit is

$$E = \text{cycle} \int P dt.$$

We may also express the  $E$  as a sum of the E.M.F.'s at the several localities, the junctions on the one hand, and the temperature-gradients in the metals on the other; so that

$$E = \Sigma(\Pi) + \Sigma(\Theta).$$

Further, as regards the  $\Pi$  function of each metal relatively to the standard

$$\Pi_{aa} = P_a T \text{ everywhere};$$

and also

$$\Theta_a = \int_1^2 \sigma_a dt;$$

so, maintaining this reference to the standard, it is still true that

$$E = \Sigma \int \Pi d \log T.$$

But  $\Pi_{ab}$ , though still equal to  $P_{ab} T$ , is no longer equal to  $T dE/dT$ , unless by  $E$  is meant  $E_{ab}$ , that is the E.M.F. of a non-existent small portion of circuit formed solely of the two metals A and B.

The fact is, that at a junction there are now three values of  $P$  and of  $\Pi$ , viz.  $\Pi_{oa}$ ,  $\Pi_{ob}$ ,  $\Pi_{ab}$ ; and it is only when we constantly maintain the reference to the standard metal  $o$  that we can say  $E = \Sigma \int \Pi d \log T$ ; otherwise there are discontinuities not allowed for. We cannot say that

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$$\int_1^2 \frac{\Pi_{za}}{T} dt + \int_2^3 \frac{\Pi_{ab}}{T} dt + \int_3^4 \frac{\Pi_{bc}}{T} dt + \dots + \int_n^1 \frac{\Pi_{yz}}{T} dt$$


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\* Cf. Phil. Mag. March 1886, pp. 271-276.

is equal to E. For one thing, the temperature-limits and the junctions do not fit. An expression of the form  $\int_{t_1}^{t_m} \frac{\Pi}{T} dt$  can still be employed for E when care is taken to arrange the  $\Pi/T$  so as to represent the difference in thermoelectric powers between pairs of points of the circuit which are *at the same temperature*, whether the metals possessing that temperature happen to be anywhere directly in contact or not. With this precaution, the integration can proceed over a discontinuity at every junction; but, in order to select the appropriate temperature-limits, either reference must be made to the real temperature of different parts of the circuit, or else the simple plan of referring everything to a hypothetical standard metal lying along the axis of temperature must be employed.

This being understood, we can still write  $\Pi/T = dE/dT$ ; but, while the E refers to the whole circuit, the  $\Pi$  does not now refer, even permissibly, to the junctions; except the hottest and coldest junctions; unless reference is made continually to the standard metal (some point of which is necessarily at the same temperature as any given junction), and not to the particular pair of metals which happen there to touch.

Hence we may not assert of the actual junctions at different temperatures that  $\Sigma(\Pi) = \Sigma(TdE/dT)$ ; nor can we assert without caution that  $\Pi = TdE/dT$  at each junction individually.

So far for a multiple metallic circuit.

If the circuit is not wholly metallic, but is partly dielectric or electrolytic, the introduction of the extraneous substance complicates matters. There may be a resultant E.M.F. now without any difference of temperature; and this E.M.F. may be partly chemical and partly physical, partly  $\Sigma(J\theta\epsilon)$ , to use the customary notation (Kelvin, 1851), and partly  $\Sigma(J\Pi)$ . For even if the temperature is everywhere uniform, it is no longer necessary for the  $\Pi$ 's to balance each other; all one can be sure of is that when there is no gradient of temperature there can be no Thomson force  $\Theta$ ; and that the resultant E.M.F. is therefore the algebraic sum of the junction forces,

$$E = \Sigma(J\Pi) + \Sigma(J\theta\epsilon).$$

It cannot now be assumed without further special proof that at any given junction  $\Pi = TdE/dT$ ; nor can we assume that it is permissible to individualise the junctions; but still, for an electrolytically closed circuit at uniform temperature, von Helmholtz has shown that taking *all* the junctions into account,

$$\Sigma(\Pi) = T \frac{dE}{dT},$$

the E being the resultant E.M.F., the sum of the contact-forces at *all* the junctions whether they be of a chemical or physical nature. And recently (Proc. Roy. Soc. Edin. Feb. 7, 1898, vol. xxii. p. 118, "On the Thermodynamics of Volta

Contact Electricity") Lord Kelvin has proved exactly the same thing to hold for a dielectrically closed circuit of uniform temperature likewise. The argument in this case he considers quite rigorous, because there is now no questionable gradient of temperature along heat-conductors, and therefore no necessarily concomitant irreversible effect; and therefore no question of whether such effect be accidental or essential.

The only loophole I can perceive for a flaw in the reasoning is the possibility that the heat of chemical combination varies for small temperature changes, *i. e.* that it is a perceptible function of the temperature; and I have no reason for pressing this, or for hesitating over accepting the above conclusion to the utmost, so long as the temperature is uniform.

It is unimportant for the present argument, but it may be worth while to notice in passing, that no such relation as  $\Sigma(\Pi) = \Sigma(TdE/dt)$  has ever been proved for a complex circuit in which differences of temperature are superposed upon other sources of electromotive force. And from what has been said in similar small type just above, no such relation can truly be asserted, without considerable care as to the form of the statement. Its most obvious signification, having reference to the actual junctions, would not be correct. It is to be observed that in the Kelvin and Helmholtz expression for a complex circuit at uniform temperature, the meaning of  $dE/dt$  is a change of E.M.F. of the circuit per degree caused by the passage of a current—caused, that is to say, by a thermal polarization: the  $dt/T$  being the efficiency of a cyclical Carnot engine. Whereas in such an expression in ordinary thermoelectricity as  $dE/dt = P = \Pi/T$ , the meaning of  $dE$  is the total E.M.F. observed in a circuit of two metals when its pair of junctions are artificially maintained at a difference of temperature  $dt$ .

It may be said that these two meanings are after all the same: and so they are in a simple circuit of two metals, but not in a complex circuit with junctions at more than two temperatures.

But what has all this to do with the localisation of E.M.F. at a given junction? Admitting, and indeed teaching, all this, I still hold that the reversible heat at a specified junction is a measure of the metallic E.M.F. located there. That in fact at a metallic junction  $e = \Pi$ , or  $J\Pi$  if anyone thinks it worth while in a matter of this sort to trouble about practical laboratory units.

Those to whom I referred in the opening paragraph of this communication make the mistake of confusing  $e$  with  $E$ ,—confusing the E.M.F. at any one junction with the whole E.M.F. in a circuit. If they do this, they naturally beg the question, and of course locate the whole E.M.F. at the particular junction which takes their fancy at the moment: usually an interface of zinc and copper.

The truth is that  $E = \Sigma(e)$  always, but only in a metallic circuit at constant temperature does  $\Sigma(e) = \Sigma(\Pi)$ ; just as

only at a metallic junction does  $e = \Pi$  individually. At an electrolytic or dielectric or what I may call a chemical junction, that is one with chemical potentialities, the E.M.F. is not purely thermal, and hence is not measured by the Peltier effect; it is chiefly of chemical origin and is calculable from the energy of combination of the materials on either side the boundary.

Observe I do not say that at such a junction there need be any chemical *action* (at least not any completed chemical combination in the ordinary sense) to account for the E.M.F., but there is the possibility of chemical combination; and there will be actual chemical combination if a finite quantity of electricity is transmitted across it. For conduction in an electrolyte is convective in its nature; whatever electricity travels, the material atoms travel with it; and the travelling of oppositely charged ions in opposite directions involves chemical action at a liquid junction, involves transfusion of substance, involves what is practically, and may be actually, chemical recombination. Possibly something of the same sort may be said, less positively, about electric displacement at a dielectric boundary.

But at a metallic junction there is no such chemical potentiality. You may pass a strong current across a zinc-copper junction for years and you will not get any brass. I would not deny that there may be a kind of material or "corpuscular" interchange even here: in fact in the light of recent most interesting work by J.J. Thomson it is probable; but the corpuscles thrown across the junction from zinc become copper; and *vice versa*, those dissociated from a copper atom settle into their new places as part of a zinc atom; there may thus be a tendency to an ineffective kind of *transmutation*, but there is no tendency to alloy. (See end of Chapter IV.)

Why then if a metallic junction is chemically inert should it ever be held that the chemical affinity of zinc for copper is the propelling influence which causes the E.M.F. located at such a junction? What has ordinary chemistry got to do with this metallic E.M.F.? I echo the question, and proceed to my second chapter.

## CHAPTER II.

### *The facts of Contact Electricity.*

Some people (for whom I have a great respect), on the strength of the fact that metals in contact attract each other, maintain that this accounts for their tendency to

combine and for their heats of combination, as well as for the value of their contact E.M.F.

Now, that metals in contact attract each other I fully admit. They must, because they are oppositely charged. There was a time when people disputed the *fact* of the Volta effect, but I am not one of those, and never was. All the facts by which Lord Kelvin or anyone else properly displays the Volta effect I fully admit, and am accustomed to show to my class; though indeed in Lord Kelvin's Friday evening Royal Institution discourse (Phil. Mag. July 1898) they are described anew with admirable clearness and precision. To avoid any possible mistake on this score, I will briefly recapitulate the facts.

Dry zinc and copper in dry air brought into contact become oppositely charged. If their surfaces are arranged so as to form a condenser of reasonable capacity, the charges may be large. When they are separated adroitly, the charges remain on the metals and raise them to a high (numerical) potential which may readily be displayed by an electrometer or even a gold-leaf electroscope.

A trace of moisture, *i.e.* of liquid electrolytic moisture, not dry vapour, may be fatal to the success of this experiment; for if a drop of liquid intervenes and connects the two metals momentarily, after the true metallic contact has been broken, nearly all their charge leaks across this conducting-bridge; and the resulting charge, and therefore the resulting potential of the separated plates, is extremely small. A water junction between two plates has no appreciable power of charging them oppositely; practically no more power than air has. In many respects a water intervention acts very like an air intervention; in one respect only does it strikingly differ:—its conductivity enables it to abolish any effective display of the opposite charges otherwise produced, *e.g.* by metallic contact. The same detrimental influence is exerted by the conductivity induced in air subjected to the action of *x*- or of uranium rays; such air behaves precisely like a badly conducting electrolyte. Nothing further need be said to make clear the action of metallic uranium for present purposes.

It is remarkable, in practice, how imperceptibly minute the quantity of liquid may be, in order thus to act detrimentally. But after all it is only a question of arithmetic:—

Let  $z$  be the average thickness of dielectric intervening between the zinc-copper plates, during their so-called close contact, everywhere except at the place where they really effectively, *i.e.* metallically, last touch as they are being

separated ; and let  $z'$  be the distance between the same surfaces at the instant when the hypothetical moist or liquid connexion is likewise last broken ; then in the dry case the resultant charge is inversely proportional to  $z$ , being in fact of the order  $\frac{r^2}{1200z}$  electrostatic units, for the usual case of circular disks ; whereas in the moist case  $z'$  must be substituted for  $z$ .

Now a very minute drop of liquid pulls out before it snaps into a column  $\pi$  tenths of a millimetre long, which then represents  $z'$  ; whereas the dry  $z$  may be a tenth or even a hundredth of this magnitude, with well-made plates and careful manipulation.

I have emphasised this to negative any possible idea that I regard moisture as an adverse fetish, acting discontinuously. It is better away ; but, if it exists, its detrimental effect is a mere arithmetical affair.

No one, I hope, can now suppose that I imagine that moisture is essential to the success of the experiment, though in his Friday evening discourse to the Royal Institution, May 1897, reprinted in the Phil. Mag. (July 1898), Lord Kelvin says that there are signs in my British Association Report (Phil. Mag. 1885) of a tendency to fall back upon De la Rive's old [and utterly discredited] hypothesis that the Volta effect was due to oxidation of the zinc by moisture from the air. He means, I expect, that I attach too much importance to the action of oxygen (which may be true : a word on that later), but never have I imagined it to be needed in the form of moisture, nor have I ever wanted the zinc to be actually oxidised. If it be perceptibly oxidised, the Volta effect is diminished.

I say once more—in accordance, I believe, with everybody :—

(1) Two metals connected wholly or partly by liquid are in approximately the same electrical condition as if connected wholly or partly by air. They do not become oppositely charged unless they are at one (or more) point metallically connected : then they do : and in order to be able fully to display this charge on separation, the persistently-connecting medium must be insulating, that is must be dry, *i.e.* free from liquid. It must also be free from high-frequency ætherial radiation or other ionising influence.

(2) If the metals are connected *both* metallically and electrolytically, metallically at one place and electrolytically at another, we have a common voltaic cell and a continuous current.

(3) To complete the statement :—If the metals are con-

nected both metallically and *dielectrically*, that is if they are insulated from each other except at one point where the intervening dielectric is swept away, we have the normal conditions appropriate for a display of the Volta effect : that is, a gradient of potential in the dielectric between them.

The safest and clearest mode of expression is what I have used : the Volta effect consists in an opposite charge acquired by dry zinc and copper while in metallic contact, a charge which results from an E.M.F. of value depending on the condition of their outer surfaces, and controlled solely by this E.M.F. and the electrostatic capacity.

I here avoid any statement involving the term metallic potential, because it is open to misconception owing to variety of definition. Some people prefer to say that zinc and copper in contact are at different potentials, whereas I prefer to say that they are at the same potential so long as they are in contact : but no one can deny that they are oppositely charged.

Some people, again, prefer to say that they are oppositely charged by reason of an E.M.F. at the junction, which keeps them at different potentials : I prefer to say that their charges are distributed so as to enable them to remain at the same potential, in spite of a difference in the specific Volta force existing at the dielectric boundary of each; in other words, that the E.M.F. is at their surface ; but again, no one can deny that there exists in the dielectric between them a gradient of potential, the natural result of their opposite charges ; which same gradient can cause a charged electrometer needle to move, even without the magnification of potential caused by separation. In fact the magnification of potential by separation does not (within limits) increase the *gradient*, for the potential rises as the capacity diminishes, and so remains in direct proportion to their distance apart, so long as that distance is moderate.

Nor can anyone deny that oppositely charged bodies, or surfaces between which there is a gradient of potential, attract each other. Hence, indirectly, a piece of zinc attracts a piece of copper with which it is at any point in contact ; and the attraction increases as the square of the potential gradient, and therefore as the square of the nearness together of the opposed or condenser surfaces.

Signor Majorana (Phil. Mag. Sept. 1899) has designed some simple methods for displaying this attraction, one of them the same as a method I had used for displaying the attraction of two metals exposed to Hertz radiation just before cohesion; viz., a fine metallic fibre hanging in front of a polished facet on a knob, the fibre and its image being watched through a

microscope (Discourse on Coherers, Journ. Roy. Inst. 1899) : but what has all this to do with the location of contact force at one junction rather than at another ? What bearing has it upon the present controversy ? So far as I see, none.

And further, I would ask, what has this dielectric attraction got to do with the heat of formation of brass ? But in asking this last question I do not pretend that it is an easy one, and I would not dogmatise as to the answer. The question is briefly treated at the end of the present chapter. I only wish to indicate at this stage that the answer to the question is open to doubt, and that it must not be taken as indisputable that the heat of combination of metals has any connexion with their voltaic force, or with their thermoelectric force either.

There was a time when I fancied that though the heat of formation of brass had no connexion with the Volta force, yet it might have some connexion with the thermoelectric force of contact, or, let us say, the Peltier effect. This idea, too, I wish to abandon\*, and for the same reason, viz., that if metallic affinity were an efficient agent in propelling the current, then I should expect the transmission of the current to result in some formation of alloy. Conceivably some secondary influence may mask the display of this result ; and if the numerical determinations of metallic heats of combination correspond, when reduced to volts, with the E.M.F. anyhow observed in connexion with circuits or partial circuits formed of those metals, that would be a striking coincidence and one to be carefully considered. So far as I am aware, no such coincidence has yet been *indisputably* discovered, even with a single pair of metals.

Experiments on heats of metallic combination have been made by Sir W. Roberts-Austen, by Dr. Galt, by Mr. F. J. Baker, and by Mr. J. B. Tayler. Doubtless also by other workers whom I forget at the moment or do not know of. The results obtained are not yet free from doubt and difference of opinion. Some of the results agree neither with the Volta nor the thermoelectric forces ; and this discordance is what I expect will ultimately be believed. On the other hand, some determinations of the heat of alloying of zinc and copper, taken in conjunction with the customary estimate of the size of atoms, do appear approximately to coincide with the order of magnitude of the Volta contact-force. (See end of this chapter.)

If this is truly so, it is very remarkable, and must greatly strengthen the ground of those commonly called "contact theorists." It would seem unlikely to be the result solely of

\* Cf. Phil. Mag. 1885, p. 356, and Journ. Inst. E. E. xiv. 1885, p. 219.

accident. On the other hand, it is undeniable that (either accidentally or otherwise) the order of magnitude of the Volta force can be calculated from the differential heats of combination of the metals for oxygen; which may be written  $(\text{Zn}, \text{O}) - (\text{Cu}, \text{O})$ . Hence, if it turns out that it can likewise be calculated from the heat of formation of brass  $(\text{Zn}, \text{Cu})$ , it will be either an odd coincidence or it will have an important chemical meaning with regard to heats of combination or chemical affinities in general.

One way of putting its meaning may be that it tends to strengthen what I may call von Helmholtz's hypothesis\*, which can be stated roughly thus:—That the metals do not really attract oxygen, nor do they really attract each other, but that what they attract is electricity; that all chemical attraction, apparently of matter for matter, is the consequence of this real attraction of matter for electricity, the atoms being electrically charged. Further, that the Volta effect is caused, simply enough, by the differential attraction of zinc and copper for electricity. The orthodox way of putting it is as follows:—The zinc attracts positive electricity most; hence, when they are put into contact, electricity flows across the junction and the zinc becomes positive and the copper negative. Another way of putting it is to say that the zinc free surface attracts negative electricity most, and accordingly pulls it in from the space around as soon as the uniformity of the force is anywhere interfered with by an inert metallic contact. In either case its ready oxidisability by negative ions is thus explained, and has not to be taken as an independent fact or basis. Whereas, then, I had proposed to calculate the Volta effect as  $(\text{Zn}, \text{O}) - (\text{Cu}, \text{O})$ , on this view it would have to be reckoned as  $(\text{Zn}, \text{E}) - (\text{Cu}, \text{E})$ ; though what is to be considered precisely as meant by E may be matter for further consideration. I am not going to say anything against this far-reaching hypothesis in a hurry. It demands separate treatment in the light of 'electron' theory.

This is what I intended when I admitted it possible that, as Lord Kelvin said, I had too great a veneration for the need for oxygen in this connexion. The sole reason why I think that it is probably the oxygen film and not the æther discontinuity which causes the force, is that its magnitude corresponds so closely, not only in order of magnitude but in relative details, with the appropriate energy of oxidation. At the same time, if the electrical attraction is the cause of oxidation tendency, this quantitative relation is not likely to afford any means of discrimination.

\* Summarised in Phil. Mag. October 1885, p. 378.

The evidence that leads Lord Kelvin to the conclusion that the æther or space or vacuum is just as effective (or ineffective) as oxygen, is derived from such experiments as those of Bottomley (see also von Zahn, &c.) to the effect that the Volta force continues unchanged in a vacuum : that an alteration of the *metals* affects its value largely, but that a change of the surrounding *medium* does not matter, unless it actually corrodes the metals and spoils them.

But this evidence derived from experiments on vacua has never seemed to me conclusive, because nothing like a real vacuum is ever attained, and even if it were, it is known with what surprising tenacity ancient air-films cling to solid surfaces ; the gaseous substance within molecular range of the solid substance being almost a part of it and not readily changed. It clings by cohesion, just as the parts of the solid substance itself cling. It is subject to Laplace's K, enormous molecular pressure. Mere exhaustion, lessening the pressure by one atmosphere, hardly disturbs it.

It was the extreme difficulty of making experiments in vacuum and substituted-media crucial that long ago deterred me from attempting them. Mr. J. Brown attempted some \* ; and now fortunately Mr. Spiers has made a brave and distinctly successful attempt in the same direction, an attempt that will, I hope, be persisted in †.

That the free or bounding surface of the metal has something to do with the Volta effect, at least in modifying its value, is proved not only by the long-known observations, say, of Ayrton & Perry, of Pellat and others, on the effect of corrosion and oxide films, but also by the interesting experiments of Mr. Erskine Murray on burnishing ‡. Simple burnishing of the parts *not* in contact can run the Volta force up considerably, from .7 volt to 1.02 volt in a certain instance ; and scratching drops it again §. But these surface-effects are admitted by Lord Kelvin, and are not thought to be even

\* Proc. Roy. Soc. vol. lxiv. p. 369 ; see also vol. xli. p. 294, and Phil. Mag. 1878, 1879, and 1881.

† Phil. Mag. January 1900.

‡ Proc. Roy. Soc. vol. lxxii. p. 113.

§ To this I should like to add that the gigantic differences of potential caused by the contact and separation of insulators, or of a metal and an insulator, *e. g.* the contact and separation of mercury or tin amalgam and glass, are very familiar ; and the great change, sometimes even of sign, caused in this potential-difference by a modification of surface, for instance by using glass whose smooth or burnished surface has been ground with sand-paper, is well known, and inevitably suggests some cause, whatever it may be, akin to that which causes a less violent but somewhat similar drop of position in a volta series when a burnished surface of zinc is scratched with sand-paper.

indirectly concerned with the zinc-copper junction and the contact-force there located\*. I should say that so great a variation, caused by a slight change of surface, shows that there is something already going on at the metal-air surface to vary. I am not aware of anything that can be done to a metal-metal junction that will affect the Volta force—except of course heating it. Lord Kelvin, however, would say, I suppose, something like this:—In a simple Volta electrostatic arrangement there are three boundaries, zinc/copper, copper/æther, æther/zinc, and there is a contact-force at each. The Volta effect observed is the sum of the three. Its seat is mainly at the zinc-copper junction; it is due to the attraction of the two metals for each other, and its value is calculable approximately from their energy of combination. The effect of any contact-force there may be at the other boundaries is to modify the observed magnitude of this true and chief Volta force. The Volta force also varies in a subordinate manner with temperature, and hence there is a minute reversible Peltier evolution of heat at the zinc-copper junction whenever a current passes. [End of hypothetical quotation.]

#### *Size of Atoms.*

The doctrine of Lord Kelvin about the energy of attraction of plates of molecular thinness approaching each other to within molecular distance and so virtually forming an alloy, though admirably ingenious, proves as it seems to me too much, *i.e.* gives too sharp an upper limit to molecular dimensions; for, as he shows with great clearness in a table in his Royal Institution discourse already often quoted, the estimate of  $10^{-9}$  cm. for molecular thinness and distance would cause the combining metals to rise to a temperature of  $7900^{\circ}$  C., or more than the probable temperature of the sun! Yet

\* The following quotation from Lord Kelvin's Royal Institution Lecture may be made:—The result of the burnishing experiments "shows that the potential in zinc (uniform throughout the homogeneous interior) increases from the interior through the thin surface-layer of a portion of its surface affected by the crushing of the burnisher, more by .32 volt than through any thin surface-layer of portions of its surface left as polished and scratched by glass-paper." If I may say so, I should express this fact in exactly the same way, viz. that the natural potential-difference between clean scratched zinc and dry air can be increased one third of a volt by burnishing its surface with a steel tool (a remarkable fact and one not easy to explain). But I should not go on, as the next sentence goes on:—"The difference of potentials of copper and zinc across an interface of contact between them is only about  $2\frac{1}{2}$  times the difference of potential thus proved to be produced between the homogeneous interior of the zinc and its free surface, by the burnishing."

there is nothing out of the way in a molecular estimate of  $10^{-9}$ . On the other hand, an estimate of  $10^{-8}$  yields a rise of temperature of  $79^\circ$ , which appears to agree very well with the order of magnitude ( $36^\circ$  Roberts-Austen,  $77^\circ$  Dr. Galt) obtained in actual experiments on the heat of formation of a zinc-copper alloy, a truly remarkable coincidence. One, however, that would be spoilt if the molecular-dimensions' estimate were only *halved*, for the theoretical rise would then be over  $300^\circ$ .

With deference I submit that the air-films, with which the metals employed in ordinary voltaic experiments are certainly coated, ought to be left on them for the data to be applicable; and in that case, when the molecular approach is made, the metals are not so much alloyed as *burnt*; so that a rise of temperature of several hundred degrees is reasonable, and a corresponding molecular estimate of say half  $10^{-8}$  is also reasonable and likely. But in the metallurgical making of brass it is not to be supposed that the metals entering into combination are coated with air-films of any importance, for their proportion of free surface is insignificantly small. Hence I think the Volta effect has nothing really to do with the making of brass.

To carry out the above combustion process, that is the voltaic approach of metallic foil of molecular thickness and its investing oxygen coat, it is not necessary to complicate matters by using *two* metals; and in the Phil. Mag. for May 1885, p. 364, I endeavoured to make a somewhat precise estimate of molecular magnitudes in this way, and even to discriminate between the molecular dimensions of different metals, since  $x$  comes out proportional to the square root of the atomic weight divided by the square root of the density and multiplied by the square root of the heat of oxidation.

### CHAPTER III.

#### *Statement of the present condition of the Controversy.*

The opposing sides of the old controversy used to be called contact theorists and chemical theorists. If this were ever a correct designation it is not the correct designation now.

There is an E.M.F. at a junction of two media, and this may be called the E.M.F. of contact, without any view as to its origin or magnitude.

This contact E.M.F. may be caused in a chemical or in a physical manner. It is generally admitted, I believe, that the E.M.F.s concerned in thermoelectricity are caused in a physical manner. It is generally admitted, I believe (I think

the statement will not be objected to in substance though its purposely crude wording may be criticised), that the E.M.F.s concerned in Volta contact electricity, as well as in ordinary voltaic electricity, are caused in a chemical manner. In saying this I am not intending any controversy, I am only trying to state. The best plan perhaps at this stage is to be more explicit.

I hold that Volta forces can be calculated, as regards their major part, from the differential energy of combination of the metals with oxygen (or other active surrounding element), and I have justified this, more or less completely, by numerical calculations (B. A. Report, 1884 ; Phil. Mag. April 1885, § 17, pp. 272, 274, &c.) based upon the great fundamental voltaic-cell paper of Lord Kelvin in 1851.

Lord Kelvin, on the other hand, holds that the Volta force can be calculated as regards its major part from the chemical affinity of metals for each other, or, to be specific, from the energy of combination of zinc with copper in the formation of brass. It is true that for the calculation to be made in this order, an estimate of molecular dimensions must be postulated, whereas his original calculation treated the order of calculation inversely; but this is of no immediate consequence, and no one at the present date has any serious compunction at including the order of ordinary molecular dimensions among data practically known.

Very well then, unless this statement be objected to, I say that the opposite camps are involved both of them in contact views, and both of them in chemical views. It is not a question of whether physical contact or some form of chemical action is operative; it is a question of which of several contacts is the really effective one, and what kind of chemical action or chemical affinity is the active cause.

Is it the contact and the chemical affinity across the metal-metal junctions, or is it the contact and chemical affinity across the metal-air junctions?

The opposite camps are thus metallic versus dielectric.

I say oxygen. Lord Kelvin scouts oxygen and says brass. He also says æther, and I am willing to say æther, too, in some sense later on, if the evidence permits; but meanwhile, it is more commonplace and safer to say oxygen: for undoubtedly oxygen is there.

Lord Kelvin does not deny the possibility, perhaps the probability, of *some* E.M.F. at the metal-air or metal-vacuum junction, which contributes to the total Volta effect, but I apprehend that he does not believe its contribution to be great. Nor, on the other hand, do I deny the existence

of an E.M.F. at the metal-metal junction, which again contributes to the total observed Volta effect, but I assert that we know its contribution to be small.

How big it is in my opinion is answered above in Chapter I. It is measured by the Peltier effect (Profs. Ayrton & Perry will here ejaculate, Stuff and nonsense! and Lord Kelvin will support them. R. I. Discourse, §§ 23 & 24.) The metal-air force is of the order volts. The metal-metal force is of the order millivolts.

Not much is known for certain about the Peltier or physical forces at metal-liquid or liquid-liquid junctions, and they are difficult to measure; but they have been partially measured by Bosscha and by Bouthy (see reference in my Report, p. 189, Phil. Mag., March 1885). They may also be theoretically estimated in the way suggested by Dr. Hopkinson in the Phil. Mag. for October 1885. M. Bouthy thinks that he has shown that the relation  $\Pi = TdE/dt$  holds at such junctions. What is certain is that if all the Peltier forces are added algebraically together in a complete circuit at uniform temperature, then, whether the completion be dielectric or electrolytic,  $\Sigma(\Pi) = TdE/dt$ ; as Lord Kelvin and von Helmholtz have proved, for the two cases of (1) dielectric medium, (2) electrolytic medium, respectively.

Thus the difference or controversy is no longer, if ever, a difference between contact and chemical action; a chemical contact seems to be admitted now by both sides, but there is an essential and by no means a nominal difference on the question of the localisation both of the E.M.F. and of the chemical contact. I locate the Volta force (the chief part of it) and the chemical contact too, at the air boundary of each metal. Anything occurring at the metallic junction I regard as physical. Lord Kelvin locates the chief part of the Volta force at what he is able to regard as an effectively chemical contact, the zinc-copper junction; and I presume that he regards whatever happens at the metal-aëther boundary as physical.

If asked why I maintain the zinc-copper junction to be chemically inert, I pass a current across it, and point to the absence of any chemical change there. If I am chaffed for over-veneration for oxygen and its nascent or potential effect on metallic surfaces, I again pass a current, by whatever means are possible, and show oxide (or more likely sulphate, this acid radical having much the same differential energy of combination with zinc and copper as oxygen has. Nor is that of chlorine very different. But one can show oxide

itself if pressed, by using a lead electrode or a copper one with an intense current).

But if told that this cannot happen always, and that the energy of combination with something (say sulphur) must be very different, I fully admit it ; but then I say that in an atmosphere of which the active ingredient is sulphur (say sulphuretted hydrogen) the Volta force will be different too. Mr. J. Brown \* has shown that it is, but the conclusiveness of the experiment is evaded by pointing to films of sulphide which introduce fresh contact-forces and complicate the circuit.

So here begins a conflict of experimental testimony and interpretation. Lord Kelvin depends on the experiments of Mr. Bottomley in a hydrogen vacuum †. I am now able to appeal to the still more elaborate and to me satisfactory experiments of Mr. Spiers (Phil. Mag. Jan. 1900). In so far as they are not conclusive, and I must assume that they are not yet rigorously conclusive, they should be repeated and improved. The research is bound to be laborious and troublesome if properly executed. I will only say, in case any young and energetic experimenter takes the matter up, that Mr. Spiers seems to me in method and motive extremely on the right track.

#### *The question of Expression in terms of Potential.*

Superposed upon the controversy as to the junction at which the main contact force really exists, there has arisen another controversy, chiefly concerned with words or modes of expression, concerning the most convenient method of defining the potential of a conductor, and especially the difference of potential between two metals.

It has been customary with certain writers, among them Professor Perry, to define the potential of a conductor as the potential of a point in the air near it,—the work that must be done to convey unit electric charge from the earth (or any place of zero potential) to a point very near the conductor ; or, better, to a point in a hollow surrounded by the conductor.

\* Phil. Mag. August 1878 *et seq.*

† Mr. Bottomley sums up thus (British Association Report, 1885, pp. 901–903) :—“The result of my investigation, so far as it has gone, is that the Volta contact-effect, so long as the plates are clean, is exactly the same in common air, in a high vacuum, in hydrogen at small and full pressure, and in oxygen. My apparatus, and the method of working during these experiments, was so sensitive, that I should certainly have detected a variation of 1 per cent. in the value of the Volta contact-effect, if such a variation had presented itself.”

I have never been able to see why these philosophers hesitate to complete the process and give the charge actually to the conductor. Why do they stop short outside? The completion of the process is so easy that precaution is needed to avoid it.

It is usually an easier matter to measure experimentally the potential of a conductor, a thing which can be connected directly by a wire to an electrometer, than it is to measure the potential of a point in air or other insulator; the latter operation requiring a water-dropper or a smoking match or an infinitely sharp point.

It has been authoritatively stated that the heterogeneous molecular structure of a metal makes it difficult to affix any meaning to the potential of an inaccessible point inside it; but if this difficulty were a real one it would surely apply still more forcibly to a heterogeneous molecular insulator. The difficulty, however, seems to me purely imaginary from any practical point of view; we need have nothing to do with the molecular structure of a metal in this connexion; by hypothesis it is a conductor, its molecules are all effectively connected, and the potential of one point is the potential of all. Nothing can be simpler than the statement that in electrostatics every part of a conductor is at one potential. We need not put on what Lord Kelvin has somewhere called a molecular microscopic binocular, and examine the atoms on all occasions.

If asked to define the potential of a metal with reference to some arbitrary standard conductor given as zero, I have only to say—the work needed to transfer a small unit charge from one to the other: or the potential energy of each unit of charge existing on the metal, provided the removal of that charge does not appreciably affect the potential: or, better,  $dW/dQ$ . Where is the difficulty? The process of charging a conductor is experimentally easy, why not introduce the process into the definition \*.

\* Nevertheless, Lord Kelvin says:—"There has been much of wordy warfare regarding potential in a metal, but none of the combatants has ever told us what he means by the expression. In fact, the only definition of electric potential hitherto given has been for vacuum or air or other fluid insulator. Conceivable molecular theories of electricity within a solid or liquid conductor might admit the term potential at a point in the interior; but the function so called would vary excessively in intermolecular space," &c. (Footnote to R. I. discourse, p. 13).

He goes on, however, "It would also vary intensely from point to point in the ether or air outside the metal at distances from the frontier small or moderate in comparison with the distance from molecule to molecule in the metal." And with this sentence I can quite agree; as well as with the bare fact stated at the end of the previous sentence.

If the potential of a metal is high, positive electricity tends to flow away from it or out of it, and does flow if a path free from obstruction is provided. If the potential of a metal is low, positive electricity tends to flow into it.

That the potential of an isolated piece of zinc is lower than the potential of an isolated piece of copper is proved (I hold) by the undoubted fact that a rush of electricity takes place from one to the other directly they are put into contact. The electricity is driven by the difference of potential : the metals may be brought near and facing each other so as to constitute the plates of a condenser of appreciable capacity ; then let them touch, and the flow automatically occurs. If potential is that which determines electrical transfer, if it be the property whose gradient is electromotive intensity, the natural statement about the previous potential of the two metals is obvious. Before contact they were at different potentials ; while they are in contact they are at the same potential. The difference of potentials is due to the unequal atomic forces straining at their frontier ; the equality of potentials is caused by the equalising electric transfer, *i. e.* to the production of charges which hold the still existing chemical forces in equilibrium. What can be simpler than this mode of expression ?

The other mode of expression says that the metals in contact are at different potentials ; meaning that the air near each is at a different potential. If that is the meaning, why not say so ? It is an undoubted fact. The step of potential in the air is experimentally demonstrable, the only question concerns the step of potential across the junction of the two metals.

To transfer a unit charge from copper to zinc in contact involves no appreciable work, whether it goes through the junction or whether it goes out and through the air\*. To transfer electricity from *near* the copper to *near* the zinc involves a definite amount of work, provided that by "near" we do not mean within molecular range; and it requires the

\* I think this is the clearest form of statement. It is possible to say there is a cyclical E.M.F. round a circuit like this with two different paths, and that the resultant force is opposed by air resistance ; but when the gradient of potential in the air is taken into account as part of the E.M.F., there is equilibrium, and the cyclical E.M.F. is zero. It is merely a question as to which is the most convenient form of expression ; there is no controversy in it : the question is touched on again at the end of the next footnote. All that I require for my purpose is the admission that no appreciable work is needed to transfer electricity across the copper-zinc junction ; while work is needed to transfer it in the air from near the copper to near the zinc.

same amount of work whether we carry it through the dielectric, or whether we plunge it into the copper and then pull it out of the zinc. If this statement of fact be not disagreed with, it is surely more convenient to say that the zinc and copper in contact are at the same potential, and that the air or space in their immediate but not molecular neighbourhood differs in potential \*. In other words, that there is a sudden step of potential in crossing the frontier from metal to air, a step which I have reckoned as about 1·8 volts up out of zinc, and about .8 volt up out of copper, and so a (roughly speaking) 1 volt gradual descent of potential in the air or space near them.

I have found in the reported discussion at the Electrical Engineers (Journ. Inst. E. E., 1885, vol. xiv. p. 233) the following ingenious and

\* It may be permissible to quote a sentence from Dr. John Hopkinson's contribution to the discussion on the same subject at the Institution of Electrical Engineers (Journal, 1885, p. 235) :—"Professor Perry defines the difference of potential between a piece of copper and a piece of zinc to be the energy required to transfer a unit of electricity from near the copper to near the zinc through the dielectric. On the other hand, as I understand the matter, Dr. Lodge, and probably Clerk Maxwell, define the difference of potential to be the energy required to transfer a current of electricity from the copper to the zinc through the junction between the copper and the zinc. Now, it appears to me that Dr. Lodge has very clearly shown that his way of looking at the matter is the more convenient; for, in the first place, it expresses, with the greatest ease, all facts that have been observed. When copper and zinc are in contact with air there is a difference of potential at the three junctions, and the sum of the three differences of potential is not equal to zero; and we have no difficulty in explaining all the electrostatic effects that we have obtained. Dr. Lodge has so clearly proved the convenience of his way of looking at the matter that it would be only wasting your time if I were to attempt to reproduce his arguments. It seems to me better to take that basis and pursue it. Now, if we take that basis as our starting-point, it is very easy to set forth all the theory of thermoelectricity, and the formulæ given at the end of Clerk Maxwell's chapter on that subject can be proved with the greatest ease; it is also easy to extend these formulæ to the case in which we have chemical action going on, and to foreshadow the precise method by which we may be able to ascertain exactly what the difference of potential is between copper or zinc or other metals and electrolytes."

He then makes some further remarks of considerable interest which were expanded by him later in the Phil. Mag. for October 1885. All I would add to the above admirable statement is that the emphasis required is upon the word "near" in the 3rd & 4th lines, and that the immediately following specification of path—"through the dielectric"—is not really essential. The potential-difference is independent of path in this case. Replacement of dielectric by electrolyte, unable to stand the potential-gradient statically, may be said to destroy equilibrium and yield a cyclical E.M.F. and a current; but, strictly speaking, the cyclical potential-difference is still zero, when resistance to steady current is taken into account; always zero, in fact, even within the variable stage, when acceleration-reaction or self-induction is likewise included.

evidently careful note added later by Prof. Perry. I will first quote it, and then paraphrase it into what I consider greater simplicity of form:

"To be quite correct, let what I have called 'tension' in a metal  $a$ , at the absolute temperature  $t$ , be denoted by  ${}_t P_a$ ; and the increase of potential from  $a$  to a metal  $b$ , as measured inductively, by  ${}_t V_{ab}$ , then the electromotive force of a thermo-electric circuit of two metals,  $a$  and  $b$ , whose junctions are at temperatures  $t_1$  and  $t_2$ , is

$$E = {}_{t_2} V_{ab} - {}_{t_1} V_{ab}.$$

The Peltier effect at a junction is

$${}_t \Pi_{ab} = {}_t P_b - {}_t P_a - {}_t V_{ab},$$

where

$${}_t V_{ab} = (k_b - k_a) t \{ T_{ab} - \frac{1}{2} t \} + C_b - C_a,$$

$${}_t P_a = \frac{1}{2} k_a t^2 + C_a.$$

$k_a$  and  $C_a$  are constants peculiar to the metal  $a$ , and  $T_{ab}$  is a constant peculiar to the two metals  $a$  and  $b$ .

Hence

$${}_t \Pi_{ab} = t \cdot \frac{d}{dt} \cdot {}_t V_{ab},$$

or the Peltier effect is proportional to the absolute temperature and to the rate of change of the contact-force with temperature."

So far the quotation; now for its interpretation.

PARAPHRASE:—Let the step of potential from inner metal to outer air across the boundary film be  $p$ , and let it be a function of temperature such that

$$p = m + \frac{1}{2} k t^2. \quad [\text{Assumption.}]$$

Let the change of potential from air near metal  $a$  to air near metal  $b$  be  $V_{ab}$  or  $V$ ; it follows that this also will be a function of the temperature. Because, if  $\Pi$  be the E.M.F. located at a junction of the two metals, the total change of potential on a journey all round from  $a$  to  $b$  and back, out *via* the air and back *via* the junction, is zero; or

$$p_a + V_{ab} - p_b + \Pi_{ba} = 0.$$

[This is only a roundabout way of saying that the Volta effect is the sum of the three junction-forces.]

Further, if we construct a complete circuit of the two metals and keep their junctions at  $t_1$  and  $t_2$  respectively, and then travel right round outside the circuit, keeping in the air near the metals, we shall encounter an E.M.F.,

$$E = V_1 - V_2.$$

[Here again there is an assumption:—viz. that the Thomson force in a metal bar, with its ends kept unequally hot, will show itself outside not as a slight gradient of potential in the air along and near the rod, but as a slight modification by temperature of the step of potential in its boundary film. This assumption is therefore quite consistent with the one made just above,  $p = m + \frac{1}{2} k t^2$ .]

Further, let us assume that  $\Pi = (k_a - k_b)t(t_0 - t)$ ; then it follows by common algebra that

$$\Pi/t = dV/dt.$$

So with all these assumptions, and all this needless and artificial attention to external occurrences, nothing is obtained beyond the admitted laws of the closed thermoelectric circuit, most simply written thus:—

$$\Pi = tf'(t); \quad E = f(t_1) - f(t_2).$$

See, for instance, my footnote to p. 270 of Phil. Mag. for March 1886, or see pp. 265, 266 of the same paper.

I trust that I have made it clear that I do not regard this matter of the definition of potential as of the same importance as the seat of E.M.F. in the pile. In no other part of this paper have I paid any attention to the wording of propositions in terms of potential ; it is a subsidiary dispute superposed on the main disagreement, which latter is in no sense a matter of words or definition.

Nevertheless the two disputes are somewhat closely allied, and the clarification of one ought to result in pacification of the other.

#### CHAPTER IV.

##### *Some recent modes of regarding the Mechanism of the Chemical Contact Force.*

I have elsewhere tried to explain the mode in which I suppose the oxygen to act to bring about that momentary transfer of electricity which occurs across the junction of two metals the instant they are put into contact. The facts postulated are (1) the fact of chemical affinity between oxygen and metal, of amount different for different metals, and (2) the fact that oxygen atoms are, at any rate some of them, negatively charged.

On the strength of these facts I see a surrounding layer of straining oxygen atoms seeking to move up to the zinc, but unable to do so because of "the impossibility of conferring an absolute charge on matter," as Faraday in his ice-pail experiment put it, or because of the "incompressibility of electricity," or because there is no avenue for the supply of electricity of opposite sign. Consequently we have a state of siege, a kind of incipient polarisation, but no charge. The zinc is somewhat in the condition of an insulated sphere surrounded by a concentric negatively charged shell, so far as the interior of the shell is concerned : outside the conditions are different. And the cause of the stress is different : there are no lines of electric force, there is no *electrical* difference of potential ; whatever force or potential-difference exists between isolated zinc and air is chemical in its nature—the result of chemical affinity. The force may be due, as Helmholtz puts it, to a specific attraction of zinc for electricity, or it may be due to a specific attraction for oxygen ; but to whatever it is due, so long as the surface is homogeneous, it is inoperative, it results in no energy transformation or work done, it is a deadlock.

Now establish connexion at one point with some neutral substance, say platinum, or a less strained-at substance, like

copper ; instantly an avenue for the relief of the strain is provided, positive electricity flows across the junction into the zinc, takes up its abode on the surface facing the oxygen atoms, the oxygen atoms approach slightly nearer all round, the surrounding molecules all round are polarised, their negative poles inwards, their positive poles outwards, a double layer is set up on the zinc, and lines of force appear all through the surrounding dielectric. These lines reach from the zinc free-surface to the copper free-surface, distributing themselves according to the ordinary rules of electrostatic capacity, and their terminations on the copper constitute its negative charge. In other words, the oxygen atoms are slightly further removed than before from the copper, and it is to that extent protected even from its previous small tendency to oxidation ; on the other hand, the oxygen atoms have approached slightly nearer to the zinc. Thus my doctrine is not a doctrine of chemical combination, but of chemical approach. The oxygen atoms approach nearer the zinc, recede further from the copper, and by these slight motions produce the whole Volta effect.

But this it may be said is nothing but a voltaic cell, except that the electrolyte is replaced by a dielectric, and so the current is momentary, not continuous. Precisely, that is my meaning.

But then, it will be objected, if a current did pass, there would be actual oxidation ; since for every electric unit that passes in a cell there must be an electrochemical equivalent of zinc oxidised. To this I agree.

Well then, pursues the objector, consider a condenser of great capacity with its alternate plates made of zinc and copper, very close together, and then short-circuit it at some point ; there will instantly be a great flow of electricity across the junction to charge the condenser, and accordingly there will be a perceptible amount of zinc oxidised. Your mere approach of oxygen atoms without combination will no longer serve.

At this point I appeal to arithmetic. The charge on an atom is of the order  $10^{-11}$  electrostatic units. The oxygen atoms immediately in so-called contact with the zinc are constituents of its condensed air-film, a film so dense as to be virtually a liquid, since it is subject to the intense molecular pressure. Not really a liquid, because it is far above the critical point, but not perceptibly differing from a liquid in density. If this be objected to, it is not essential to my argument, because there is plenty of margin ; only it seems to me likely to correspond roughly with the truth. The

number of atoms per square centimetre in the layer facing the zinc will therefore be of the order  $10^{16}$ . Of these only a portion will be oxygen ; and probably it may be said that only a small proportion are ionised and so open to combination. But as I do not need combination, I see no necessity to postulate ionisation, or to care what proportion are in this condition. Certainly I need molecules capable of being polarised electrically, but that at the present date will hardly be denied to any material molecules whatever.

Very well then, if for any reason polarisation takes place, the surface-density of the charge on either face of the double layer can be  $10^{16} \times 10^{-11} = \sigma = 10^5$  electrostatic units per square centimetre, at a maximum. The mechanical tension across the layer is  $2\pi\sigma^2$ , and the intensity of electric field there is  $4\pi\sigma$ , which is also the gradient of electric potential.

Now the thickness of the layer is of molecular dimensions,  $10^{-8}$  centim. say ; hence the difference of potential between its faces, that is the difference of potential between the zinc and the air in its neighbourhood, is  $4\pi\sigma z$ , which is of the order ( $12 \times 10^5 \times 10^{-8} = 10^{-2}$ ), one-hundredth of an electrostatic unit, or 3 volts. Now plainly this is of the right order of magnitude. The Volta effect observed *can* be explained by such an electrical double layer, by such a chemical layer of straining oxygen atoms, at a metallic surface \*.

That it can be equally well explained for metals in absolute vacuum or free æther I would not presume to deny ; but I cannot do the arithmetic for that case, because of an utter lack of data. It is to be observed, however, that the only gaseous or material substance needed (other than metal) is the coherent film on the surface ; all the rest of the gas is merely a dielectric medium for the transmission of electrostatic induction or lines of force, and for this function an absolute vacuum serves perfectly. Consequently, merely removing the plates into the receiver of an air-pump will make no practical difference.

But still, so far, I have not met the hypothetically suggested difficulty about the condenser of large capacity and the amount of real chemical action needed to account for the current required to charge it to the voltaic difference of potential.

We have only to proceed with the calculation.

The condenser formed by the opposing surfaces of zinc and copper is a condenser of the same (or comparable) area to that molecular condenser just postulated between either metal and the air. The only difference is that these last are of molecular thinness, whereas the condenser formed by well-

\* See also a footnote to p. 379 of a paper in the Phil. Mag. for October 1885, where I reckoned practically the same thing.

fitting plates of zinc and copper is of a moderate thinness,  $z$ , say the hundredth part of a millimetre, or something of that order.

Hence, when the plates are approached from infinity to this distance  $z$ , and are put into contact to establish the state of polarisation, there will be a rush of charge out of the molecular condensers into the newly formed condenser ; for they are condensers in series, and every unit gained by one must be lost by the other.

But since the molecular condensers are to retain their original potential-difference, this supply of electricity can only be given by a change in capacity, *i.e.* a change in their molecular thickness  $x$ , such that

$$-\frac{dx}{x^2} = \frac{1}{\infty} - \frac{1}{z},$$

or

$$dx = \frac{x^2}{z} = \frac{10^{-16}}{10^{-3}} = 10^{-13} \text{ cm.,}$$

the hundred-thousandth part of molecular magnitude.

Thus the diminution in thickness of the superficial double layer, or the approach of the oxygen atoms, in an extreme case, has only to be a hundred-thousandth part of their whole distance. This can hardly be called chemical combination : indeed it is a scarcely perceptible chemical *approach*.

Put in another way it amounts to this : that if the oxygen atoms varied their distance from the zinc and the copper respectively (one decreasing, the other increasing) by so much as a tenth of 1 per cent., the electricity so set free or transferred from one surface to the other would be able to charge an ordinary condenser of the same area in the intervening space to a density of 100 c.g.s. ; which is considerably more than ordinary air can stand.

The only way to get a perceptible amount of real oxidation, that is an approach over the whole molecular distance, is either to bring the condenser plates themselves within molecular distance of each other, which would squeeze out the films and modify the whole action, or else to bring them within molecular distance of different parts of one and the same liquid conductor (so that the whole strain is thrown upon the molecular film-condensers and none upon any intervening material) ; and this is exactly what is done in an ordinary voltaic cell.

[To be continued.]

**XXXIV. The Echelon Spectroscope; with Application to Investigate the Behaviour of the chief Lines in the Mercury Spectrum under the Influence of a Magnetic Field.** By Lord BLYTHSWOOD and Dr. E. W. MARCHANT, Granville Scholar of the University of London\*.

### § 1. Introduction.

IT has been thought that it might be of interest to publish some account of the mounting adopted in the Blythswood Laboratory for the echelon diffraction-grating (invented some two years ago by Prof. Michelson †), and to describe the method adopted for the determination of what may be called the constants of the instrument.

The echelon grating in use here was by Hilger and was the first made in this country. It consists of fifteen plates each about 7·5 mm. thick, made of light flint-glass, set originally with 1 mm. steps, but afterwards altered so as to make the steps only ·5 mm. wide.

### § 2. Method of Mounting.

The mounting was adapted so as to make use of the telescope and collimator belonging to a large goniometer already in use in the laboratory. The telescopes in question had object-glasses of 28 inch focus and 2 inch aperture ‡.

In order to obtain the necessary preliminary dispersion a small solar spectroscope was employed, having movable dispersion- and back-reflexion prisms, so that both the telescope and collimator were fixed. This form of instrument is exceedingly convenient when the source of light cannot easily be shifted.

A diagram and photograph of the arrangement are given in fig. 1.

The telescopes  $T_1$  and  $T_3$  are first set so that the slits  $S_1$ ,  $S_2$  are in the solar foci of their respective object-glasses.

The instruments are then so set relatively to each other, that the spectrum from the solar spectroscope focusses exactly on the slit  $S_2$ . In order to get any particular line of the spectrum on the slit  $S_2$ , the handle  $H$  is turned (thus

\* Communicated by Lord Kelvin.

† Astrophysical Journal, vol. viii. No. 1, p. 36, June 1898.

‡ When the mounting is made complete for the instrument, it is advisable to have short-focus glasses (say 6 in. or 8 in.), with the same aperture, so as to get as much light as possible.

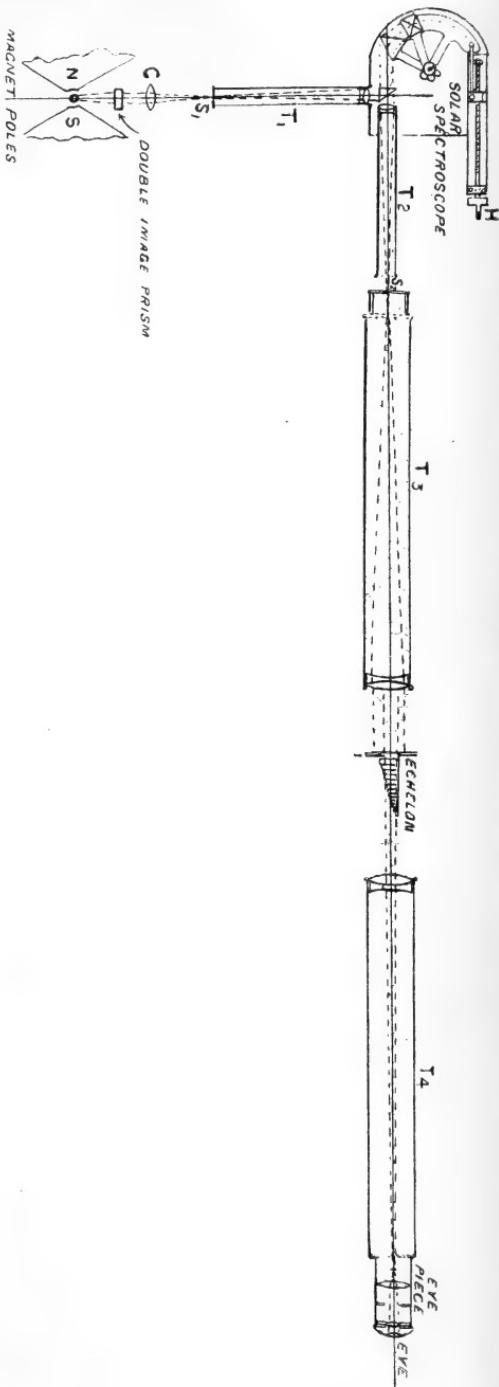
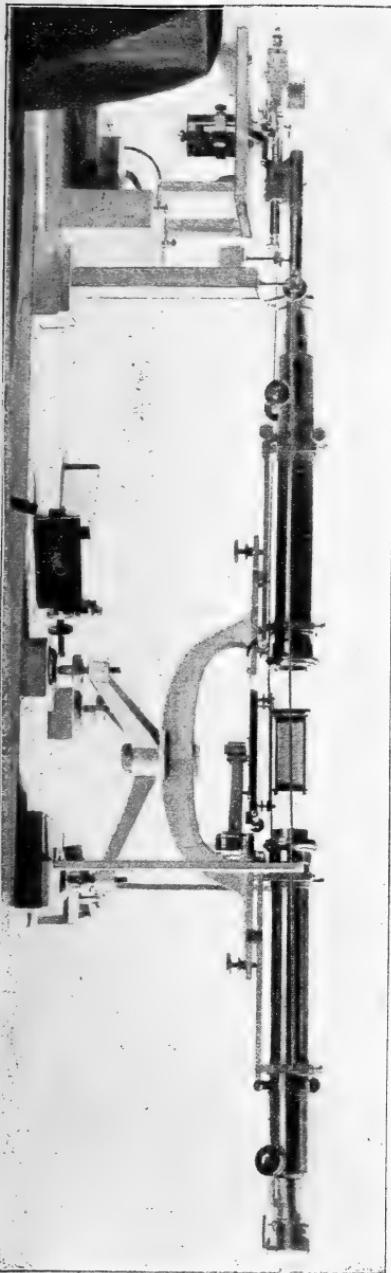


Fig. 1.



moving the prisms) until the required line appears in the field. In order to do this easily a long rod was attached to the handle H, which could be turned by the observer at the eyepiece: this rod appears in the photograph together with a similar rod for opening and closing the slit S<sub>2</sub>.

The condensing-lens C is used to focus the source of light (shown between the poles of a magnet) on the slit S<sub>1</sub>. All these adjustments are made with the echelon out of position. In order to obtain the best possible results with the instrument, the slits S<sub>1</sub>, S<sub>2</sub> should both be set parallel to the steps of the echelon. The easiest way, of course, of doing this is to make both the slits and the edges of the echelon as nearly vertical as possible. The instrument is, however, nothing like so sensitive to this adjustment as the concave gratings with 14,000 or more lines to the inch.

When the adjustment is complete and the particular line which it is required to examine is focussed on the slit S<sub>2</sub>, the echelon may be placed in the path of the beam. It should be noticed that the focus of the orders when the echelon is in position is not necessarily the same as that for the slit S<sub>2</sub> when the echelon is removed. In this particular instrument, owing to some error in the plates, the focus was obtained when the eyepiece was about an inch further out than it was with the slit S<sub>2</sub> sharply focussed, with the echelon removed.

In the mounting used here a form of parallel motion was adopted for moving the echelon in and out of position; in setting, therefore, the echelon was moved across the field until the brightness of the lines seen in the eyepiece was a maximum. When once this position had been determined, marks were made on the stand and the echelon-mount, so that the grating could always be placed in that position.

There was one other motion of which the grating was capable, viz., a rotation round a vertical axis in the centre of its stand: this motion could be effected by a screw, with a counter spring for obtaining the motion in both directions. The use of this adjustment is explained later. Finally, the echelon was placed on a stand with levelling-screws, so that the edges of the plates could be set exactly vertical. (See above.)

### § 3. *Constant of the Grating.*

As stated above, the grating was made of a light flint-glass, the refractive index of which was given by the Jena manufacturers for five principal wave-lengths. From three of these values the values of the constants in Cauchy's expression for the refractive index were worked out; the resulting equation

obtained for this glass was as follows:—

$$\mu_\lambda = 1.5958 + \frac{8.03 \times 10^5}{\lambda^2} + \frac{1.53 \times 10^{12}}{\lambda^4},$$

where  $\lambda$  is expressed in  $10^{-10}$  metres.

From this equation interpolated values of the refractive index for other wave-lengths were calculated, and a curve plotted, as shown in fig. 3 (p. 389).

The value of  $d\mu/d\lambda$ , which it is also necessary to know for different wave-lengths, was obtained from the equation

$$-d\mu_\lambda/d\lambda = \frac{16.06 \times 10^5}{\lambda^3} + \frac{6.12 \times 10^{12}}{\lambda^5},$$

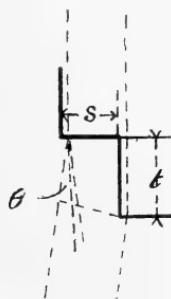
where, as before,  $\lambda$  is expressed in  $10^{-10}$  metres.

A curve for this was also plotted, and is shown in fig. 3.

The thickness of the echelon plates was carefully measured by means of a measuring micrometer reading to  $1/10,000$  of an inch, and was found to be  $7.424 \pm .006$  mm.; this accuracy being sufficient for all measurements made with the instrument.

We may now consider the expressions obtained for the dispersion of the instrument\*.

Fig. 2.



If  $m$  be the order of the spectrum of the light observed,

$\theta$  " angle of deviation from the normal,

$\lambda$  " wave-length of the light,

$\mu$  " refractive index of the glass for the wave-length considered,

$t$  " thickness of the echelon-plates,

$s$  " width of a step:

the retardation produced by each step of the echelon (fig. 2)

$$\delta m\lambda = \mu t - t \cos \theta + s \sin \theta. \quad \dots \quad (1)$$

Approximately  $m\lambda = (\mu - 1)t$ , since  $\theta$  is very small.

\* Michelson, *Astrophys. Journ. loc. cit.*

By differentiation with respect to  $\lambda$  we have, after putting  $\sin \theta = \theta$  and  $\cos \theta = 1$ ,

$$md\lambda = t(d\mu/d\lambda)d\lambda + sd\theta. \dots \dots \dots \quad (2)$$

By differentiation with respect to  $m$  we have

$$\lambda dm = sd\theta. \dots \dots \dots \quad (3)$$

Eliminating  $s$ , and putting  $dm = 1$  so that

$\delta\theta_1$  = angular dispersion between two lines whose difference in wave-length is required;

$\delta\theta_2$  = angular dispersion between two successive orders, we have

$$\delta\lambda(m - td\mu/d\lambda) = \lambda \frac{\delta\theta_1}{\delta\theta_2}. \dots \dots \dots \quad (4)$$

Substituting for  $m$  the approximate value  $(\mu - 1)t/\lambda$ ,

$$\delta\lambda = \frac{\lambda^2}{t((\mu - 1) - \lambda \frac{d\mu}{d\lambda})} \frac{\delta\theta_1}{\delta\theta_2}.$$

The value of  $\lambda^2/t((\mu - 1) - \lambda \frac{d\mu}{d\lambda})$  can be calculated from the known refractive index of the glass; and this constant being known, the difference in wave-length between two lines seen in the echelon may be determined, if their dispersion relative to the distance between two successive orders be known. It is to be noted that this constant is quite independent of the width of the steps, and is therefore a constant for the echelon, however it is put together. The only necessary condition is that the instrument shall not be much tilted, *i. e.* that the light shall pass through it in a direction nearly normal to the plates. The values of this constant were calculated for a series of different wave-lengths and a curve plotted, as shown on fig. 3 ( $k_1$ , 3). The expression  $1/t((\mu - 1) - \lambda d\mu/d\lambda)$  is much more nearly a constant for the gratings, and for the observation of the Zeeman effect is useful in giving at once the value of  $\delta\lambda/\lambda^2$  corresponding to a dispersion  $\delta\theta_1$ .

Thus

$$\frac{\delta\lambda}{\lambda^2} = \frac{1}{t((\mu - 1) - \lambda \frac{d\mu}{d\lambda})} \frac{\delta\theta_1}{\delta\theta_2}.$$

The curve for this expression is also shown in fig. 3 ( $k_2$ , 4).

## the Echelon Spectroscope.

Curves showing relation between Wave-length and  
Refractive Index of Glass.

$$\mu = 1.558 + 8.03 \times 10^5 / \lambda^2 + 1.53 \times 10^{12} / \lambda^4.$$

Value of  $-(\delta\mu/\delta\lambda) \times 10^5$ .

$$-\delta\mu/\delta\lambda = 16.06 \times 10^5 / \lambda^3 + 6.12 \times 10^{12} / \lambda^5.$$

Value of  $K_1$ ,

$$K_1 = \lambda^2 / \varepsilon \{(\mu - 1) - \lambda \delta\mu/\delta\lambda\}. \quad \delta\lambda = K_1 \delta\theta_1 / \delta\theta_2,$$

where  $\delta\theta_1$  = dispersion between lines whose difference in wave-length is required,  
 $\delta\theta_2$  = dispersion between two consecutive orders.

Value of  $K_2$ ,

$$K_2 = [1/\varepsilon \{(\mu - 1) - \lambda \delta\mu/\delta\lambda\}] \times 10^3,$$

and

$$\delta\lambda / \lambda^2 = (K_2 \delta\theta_1 / \delta\theta_2) \times 10^{-8},$$

with same notation as in (3).  $\lambda$  is expressed in  $10^{-10}$  metres.

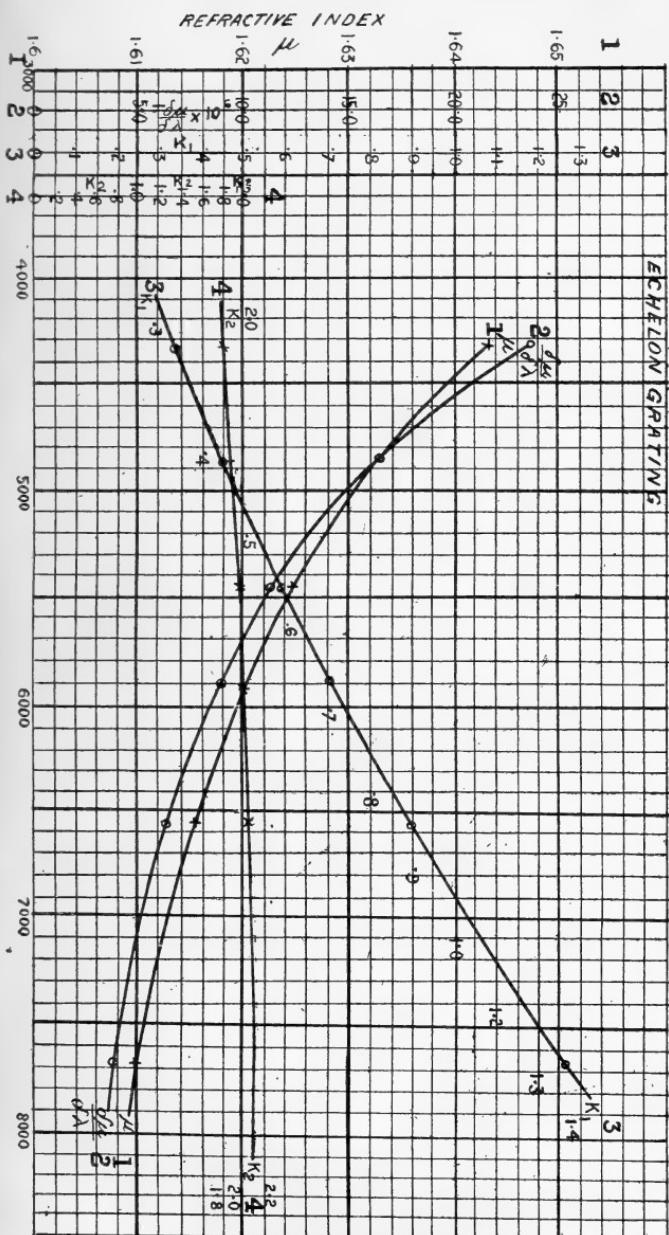


Fig. 3.  
Wavelength in  $10^{-10}$  met.

#### § 4. Method of Using the Grating.

The apparatus having been set as described in § 2 (*Method of Mounting*), the echelon-mount and the whole instrument having been carefully levelled, the line which it is required to examine is set on the slit  $S_2$  of the echelon-mounting. The echelon having been slipped into position and adjusted as described, several possible conditions may be observed in the eyepiece.

Taking first the case of a line which is not split up under the resolving power of the echelon, there may be one bright single line visible, together with (if the light be very bright) a series of lines gradually diminishing in intensity as the distance from the central line is increased; or there may be two lines of equal intensity with other lines gradually diminishing in intensity towards the edge of the field; obviously there are numerous other intermediate conditions possible, in which one line is brighter than the other. The lines of gradually diminishing intensity are the successive orders of the grating for this particular light.

The position of the grating in which two equal lines or orders are visible in the field may be described as that giving the double-order condition. The corresponding position in which only a single line or order is visible may be described as the single-order condition.

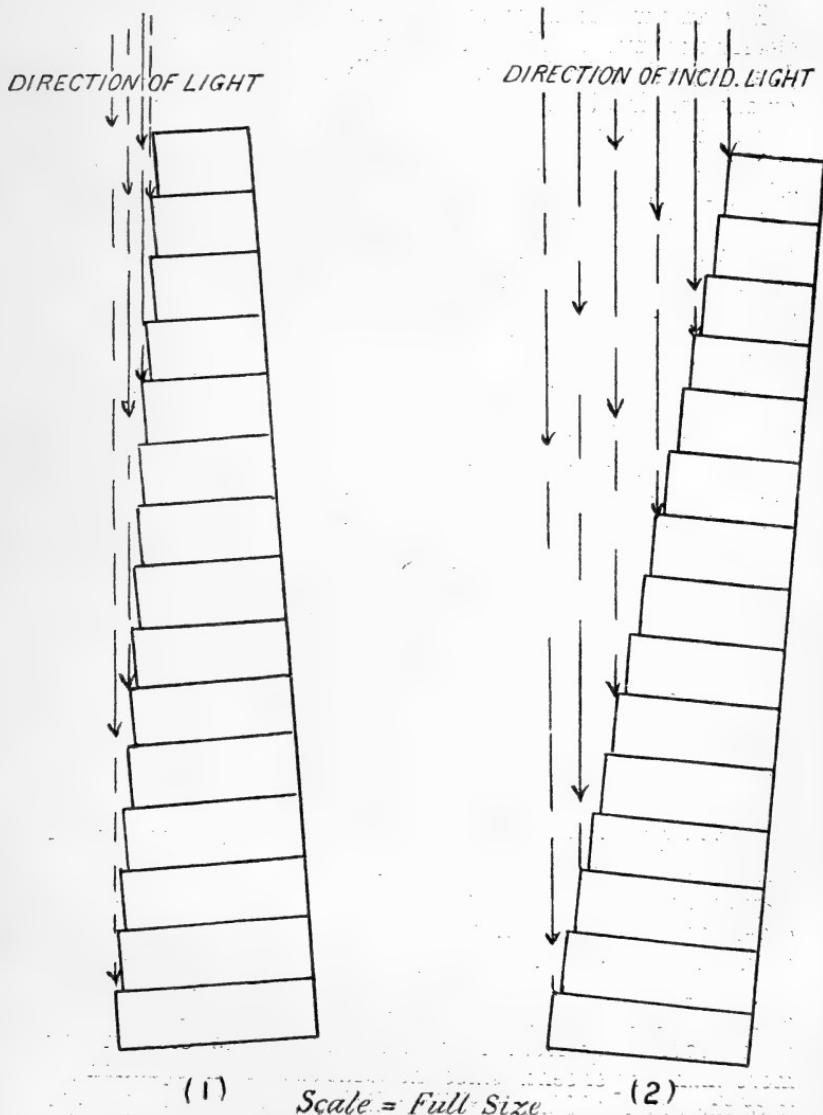
By turning the grating slightly round its central vertical axis it will be found that, say from the single-order position, another order will appear to one side of the single line, and gradually increase in intensity until the two lines or orders are equal: if the turning be still further continued, the original line will fade and the new line will get brighter, and at the same time will move towards the centre of the field until we have the original single-order condition with the new order.

It will be found, when the echelon is turned from a position slightly tilted in one direction to a position slightly tilted in the other direction, that there is a certain position in which, whatever way the echelon be turned, the order on the left-hand side, say (in the eyepiece), will always brighten. In any other position, of course, by tilting the echelon one way the order on the right of the original brightens, while an opposite tilt will brighten the order on the left. This condition corresponds to the position of the echelon in which the plates are normal to the incident light.

It will also be found that when the position of the echelon described above (which may be called the direct position) has been obtained, a tilt in one direction will rapidly diminish the

intensity of the lines, and increase the distance between two successive orders, while a slight tilt in the other direction will have very little effect either on the intensity of the lines or on the dispersion of the orders. The explanation of this effect is at once seen when we consider the effect of tilting the instrument.

Fig. 4.



In position 1 (fig. 4) the steps overhang each other, as it were, and their effective width is rapidly diminished.

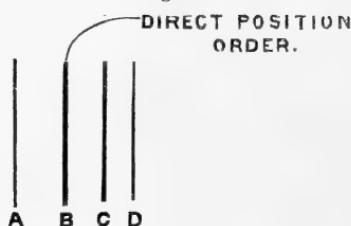
If  $\theta$  be the angle of tilt, the effective width of a step  $= s \cos \theta - t \sin \theta$ , where  $s = .5$  mm. and  $t = 7.5$  mm. q. p. A tilt of one degree, therefore, will reduce the effective width of a step to .75 of its original value.

In position 2 (fig. 4) the width of the steps is only reduced to  $s \cos \theta$ , where  $\theta$  is the angle of tilt, and  $\cos \theta = 1$ , when  $\theta$  is small.

The amount of light passing through the instrument is clearly not much affected. A tilt of one degree in this direction will only diminish the effective width of the steps by one part in 5000. As is shown later, a tilt of one degree is approximately that required to obtain the double-order condition from the single-order condition, or *vice versa* with yellow light.

It has generally been found best to work with the order next to that obtained in the direct position, or even the second order from that position. When working in the equal-order condition, it is best to work with the first and second orders away from the direct position. If the direct-position order was used, it was found that the dispersion of the order, say, to the left of the direct-position order (the direct-position order being supposed to be the left-hand one) was not equal to that of the order to the right of the other equal order. In fig. 5 the distance A B was not equal to the distance D C. This would introduce uncertainties in the measurements.

Fig. 5.



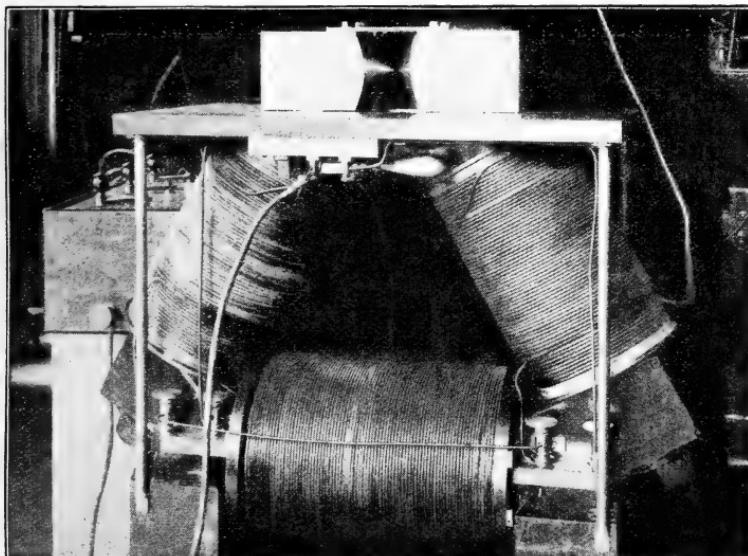
It should be noticed that the direct position is not necessarily that in which only a single order is showing brightly; it may be a position when two equal orders are showing, or two orders one brighter than the other, this depending entirely on the retardation produced by the plates of the echelon for the particular light under examination. The effect of not working with the direct-position order, but with, say, the third order away from it, will not affect the constant by more than .06 per cent., since the value of  $m$  in the equation (2) is of the order 5000 for yellow light. Or, considering the change in the amount of retardation produced by tilting the

plate, for example one degree, the thickness of glass traversed is only increased by one part in 10,000, or .01 per cent. Since the retardation is increased by one part in 10,000 and the original retardation is 5000 wave-lengths, the increase in retardation is approximately half a wave-length; this amount of tilt, therefore, is that required to obtain the double-order condition from the single order. If we increase the tilt to 1.5 degree, the retardation is increased approximately to one part in 5000; and we should obtain, therefore, the single-order condition again, but with the 5001st order.

### § 5. *The Magnet.*

Before proceeding to a consideration of the results obtained of the Zeeman effect, some mention may be made of the magnet used in these experiments. A photograph of it is given in fig. 6.

Fig. 6.



The pole-pieces were 5 inches square, and were turned down to a cone whose semi-angle was  $60^\circ$ , with a flat .5 inch in diameter at the tips. When viewing along the lines of force, one of the pole-pieces used was bored out, the hole being .5 inch in diameter at the tip and .75 inch towards the outer face.

With a current of 20 amps. (which did not heat the coils excessively), a field of about 24,000 c.g.s. units was obtained across an 8 mm. air-gap. When the air-gap was reduced to 1 mm., a field of 40,000 c.g.s. units was obtained.

In these experiments, however, it was impossible to use a gap of much less than 8 mm., on account of the size of the capillary of the vacuum-tube used to obtain the mercury spectrum.

With the hollow pole-pieces the maximum field was about 16,000 c.g.s. units with an 8 mm. gap.

The field-strengths were measured by means of a small coil whose area had been carefully determined electrically, by comparison with a standard single-layer coil wound on a core of measured diameter. This coil was used in conjunction with a ballistic galvanometer which had been standardized by means of the discharge from a 5 M.F. condenser charged to a known potential. The P.D. to which the condenser was charged was measured by an Evershed voltmeter calibrated by the potentiometer method with a Clark cell.

#### § 6. *Results obtained of the Zeeman Effect on the Chief Lines of the Mercury Spectrum.*

We may now consider some of the results obtained with this instrument in the observation of the Zeeman effect on the chief lines of the mercury spectrum.

Attention was mainly directed to the blue (4358) line and the green (5460), since these could both be photographed. The blue line (fig. 7) photographed fairly easily, the exposure necessary being from 10 to 20 minutes. The green line (fig. 10) on the other hand, though very bright visually, generally required about two hours' exposure. The other lines examined were the two yellow lines ; but no good photographs were obtained. Measurements on them were made with a micrometer-eyepiece.

In photographing and observing these lines, it is very important that the tube should give a brilliant light. In order to ensure this, fresh tubes were continually used, the exhaustion being generally carried to 1 mm. or less. A drop of mercury was put into the tube to give the requisite mercury-lines. The tube was kept heated by a spirit-lamp placed underneath it ; the lamp at the same time heated the iron of the pole-tips. The alteration in the magnetic flux caused thereby was measured, and was found not to exceed 1 per cent.

We may first consider the behaviour of the blue (4385) line. Photographs are given, taken both in the single- and double-order conditions.

Fig. 7.—Blue (4358) Line of Mercury.

Single Order.



Without Magnetism.

Double Order.



Viewed across the Lines of Force.

Magnetic Field = 5000 c.g.s. units.



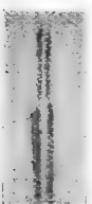
Magnetic Field = 12,000 c.g.s. units.



Magnetic Field = 24,000 c.g.s. units.



Magnetic Field = 23,800 c.g.s. units.

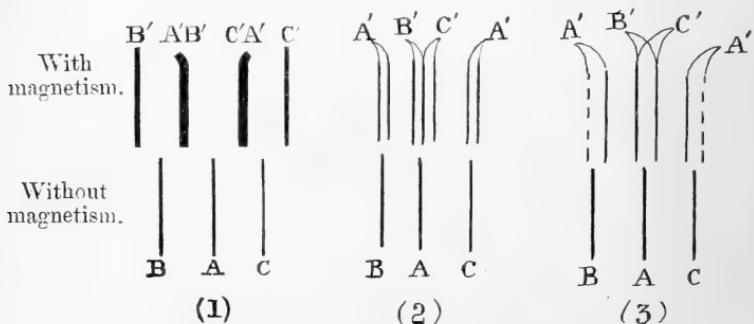


A double-image prism was employed to separate the outer and inner components of the compound line. In the photographs, components which are polarized parallel to the lines of force form the top half of the line, and components polarized perpendicularly to the lines of force are at the bottom.

Under a weak magnetic field the line appears as a triplet; as the strength of the field increases the lower or inner component splits into a doublet, and the line becomes a quartet. It should be noticed that in the double-order condition the central line, which is composed of two outer components of the two orders nearly superimposed, is very much brighter than the outer components.

In the single-order photograph with a slightly stronger field (12,000), the side components of the orders on each side of the original single order have come near enough to the centre of the field to become bright, and are superimposed on the components due to the original single order. In a still stronger field the two outer components split into two components each so that the resultant line becomes a sextet. It is somewhat difficult to follow the final splitting of the outer components. It may, however, best be done from the single-order condition.

Fig. 8.



Starting from the condition (1) fig. 8, which is that shown in the photograph with a field of 12,000 c.g.s. units, the line  $C'$  due to the order  $C$  is superimposed on the line  $A'$  due to  $A$ ; and similarly  $B'$  is superimposed on the other component of  $A$ , both lines being thick. As the field-strength increases, the components of  $A$  get farther from the centre of the field, and finally fail to show on the photograph; the right-hand component of  $B$  and the left-hand component of  $C$  gradually get nearer the centre of the field and become

brighter, and cleanly split, each into two lines. Next we have the outermost right-hand component of B, coincident with the outermost left-hand component of C as in (2), fig. 8, with a magnetic field of 21,800.

With a still stronger field (23,800) the components of B and C coincide with each other; this is shown in (3) and also in the photograph. In this way we are able to trace out the gradual resolution of the original line.

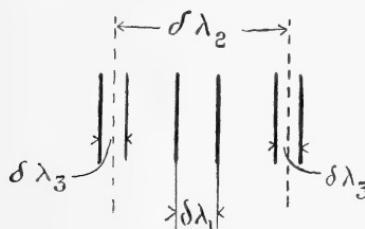
The line therefore becomes a sextet, the relative separation of the components being shown below.

$H$  = strength of the magnetic field.

$\delta\lambda_1$  is the difference in wave-length between the two inner components of the sextet.

$\delta\lambda_2$  is the mean difference in wave-length between the outer components.

$\delta\lambda_3$  is the difference in wave-length between the components of the outer components of the sextet.



$$\lambda = 4358 \cdot 10^{-10} \text{ metres.}$$

$H$ .	$\delta\lambda_1$ .	$\delta\lambda_1/H \times 10^6$ .	$\delta\lambda_2$ .	$\delta\lambda_2/H \times 10^6$ .	$\delta\lambda_3$ .	$\delta\lambda_3/H \times 10^6$ .
5,000	.....	.....	.143	28·6	.....	.....
12,100	.104	8·5	.341	28·2	.....	.....
12,900	.112	8·7	.360	28·0	.052	4·2
20,000	.166	8·3	.580	29·0	.098	4·9?
21,300	.176	8·3	.60	28·2	.09	4·2
23,400	.200	8·6	.68	28·8	.098	4·2

These values have also been confirmed by photographs taken along the lines of force. As might have been expected from theoretical considerations, the line first splits into a doublet, and in a stronger field the doublet splits up into a quartet exactly corresponding to the outer quartet of the line viewed across the lines of force.

The values obtained are given below:—

$H$ .	$\delta\lambda_2$ .	$\delta\lambda_2/H \times 10^6$ .	$\delta\lambda_3$ .	$\delta\lambda_3/H \times 10^6$ .
3,550	.098	27·8	.....	.....
8,700	.246	28·4	.....	.....
15,600	.435	27·8	.075	4·8?

The mean values obtained from these measurements therefore give :—

$$\frac{\delta\lambda_1}{H} = 8.5 \times 10^{-6}, \quad \frac{\delta\lambda_1}{\lambda^2 H} = 4.5 \times 10^{-13},$$

$$\frac{\delta\lambda_2}{H} = 28.3 \times 10^{-6}, \quad \frac{\delta\lambda_2}{\lambda^2 H} = 14.95 \times 10^{-13},$$

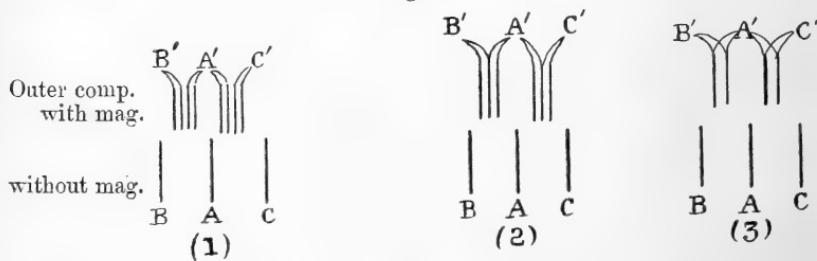
$$\frac{\delta\lambda_3}{H} = 4.3 \times 10^{-6}, \quad \frac{\delta\lambda_3}{\lambda^2 H} = 2.28 \times 10^{-13},$$

$\lambda$  being expressed in  $10^{-10}$  metres.

The green line of mercury (5460) behaves somewhat differently under the action of a magnetic field. With a weak field of about 6000 c.g.s. units the line splits into a triplet, as shown in the photographs, both with single and double orders.

As the field increases in strength the inner component of the line, which is perceptibly broadened under the weak field, splits into a triplet, at the same time each of the outer lines splits into a doublet, the resultant being a septet. The single-order photograph shows the line as it ultimately appears in the strong field. It is to be noticed, however, that the outer lines are really due to three orders.

Fig. 9.1



In fig. 9 (1) represents the appearance under a field of about 16,000 units; (2) shows the condition under a slightly stronger field, the centre line of the inner three being due to the coincidence of the outermost components of the orders. In (3) (the condition shown in the photograph with a field of 20,000 units) the lines completely overlap. Conditions (1) and (2) are well shown in the photograph of the green line taken along the lines of force. At the top and bottom of the line, nearer the edges of the hole in the pole-piece, the field is considerably stronger than at the centre. At the ends of the line, therefore, we have the condition shown at (2), at the centre of

Fig. 10.—*Green (5460) Line of Mercury.*

Single Order.

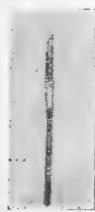


Double Order.

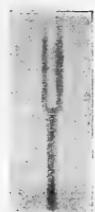


Without Magnetism.

Viewed across the Lines of Force.



Magnetic Field = 6000 c.g.s. units.



Magnetic Field = 19,800 c.g.s. units.

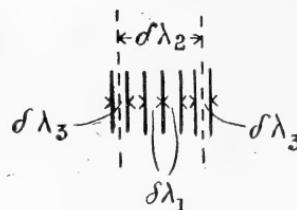
Viewed along the Lines of Force.

Magnetic Field at Centre = 13,000 c.g.s. units.



the line we have condition (1). In the photograph, however, two equal orders were showing when there was no magnetism; and there is therefore only one group of lines in the centre of the field, instead of the two groups shown in the diagram.

Below are given the results of the measurements made with this line.



$$\lambda = 5460 \text{ tenth-metres.}$$

H.	$\delta\lambda_1$	$\delta\lambda_1/H \times 10^6$	$\delta\lambda_2$	$\delta\lambda_2/H \times 10^6$	$\delta\lambda_3$	$\delta\lambda_3/H \times 10^6$
12,900	.981	6.3	.416	32.3	6.082	6.4
17,800	.....	.....	.588	32.9	.124	6.9
20,000	.133	6.6	.....	.....	.....	.....
23,000	.....	.....	.74	32.3	.156	6.8
23,400	.156	6.7	.....	.....	.....	.....

#### Along the lines of force.

8,700	.....	.....	.282	32.5	.....	.....
13,000	.....	.....	.415	32.0	.085	6.5

The mean values obtained from these measurements give :—

$$\frac{\delta\lambda_1}{H} = 6.5 \times 10^{-6}, \quad \frac{\delta\lambda_1}{\lambda^2 H} = 2.3 \times 10^{-13},$$

$$\frac{\delta\lambda_2}{H} = 32.4 \times 10^{-6}, \quad \frac{\delta\lambda_2}{\lambda^2 H} = 10.9 \times 10^{-13},$$

$$\frac{\delta\lambda_3}{H} = 6.6 \times 10^{-6}, \quad \frac{\delta\lambda_3}{\lambda^2 H} = 2.22 \times 10^{-13},$$

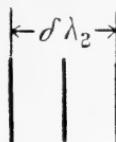
$\lambda$  being expressed in  $10^{-10}$  metres.

Measurements were also made on the yellow (5768) line.

This line splits into a pure triplet viewed across the lines of force, and into a corresponding doublet when viewed along the lines of force. Under the strongest field there appeared to be no tendency for these lines to split further. The difference in wave-length between the outer components was measured with a micrometer-eyepiece.

The results of the measurements are given below; for the

sake of uniformity the difference in wave-length between the outer lines of the triplet is called  $\delta\lambda_2$ .



$$\lambda = 5768 \times 10^{-10} \text{ metres.}$$

H.	$\delta\lambda_2$ .	$\delta\lambda_2/H \times 10^6$ .
5,500	.182	33.2
12,900	.441	34.0
23,400	.768	33.1

Along the lines of force.

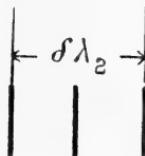
8,700	.294	33.9
13,000	.434	33.4

These measurements give a mean value

$$\frac{\delta\lambda_2}{H} = 33.4 \times 10^{-6}, \quad \frac{\delta\lambda_2}{\lambda^2 H} = 10.0 \times 10^{-13}.$$

where  $\lambda$ , as before, is expressed in  $10^{-10}$  metres.

A similar series of measurements was made on the other yellow (5790) line of mercury. This also splits into a pure triplet, but the value of  $\delta\lambda_2/H$  is smaller than that obtained with the other yellow (5768) line. The results of these measurements are given below.



$$\lambda = 5790 \times 10^{-10} \text{ metres.}$$

H.	$\delta\lambda_2$ .	$\delta\lambda_2/H \times 10^6$ .
5,500	.167	30.5
12,900	.405	31.3
22,300	.669	30.0

Along the lines of force.

8,700	.266	30.6
13,000	.409	30.8

This gives a mean value

$$\frac{\delta\lambda_2}{H} = 30 \cdot 6 \times 10^{-6}, \quad \frac{\delta\lambda_2}{\lambda^2 H} = 9 \cdot 13 \times 10^{-13},$$

$\lambda$ , as before, being expressed in  $10^{-10}$  metres.

It will be noticed that the value of  $\delta\lambda_2/H$  for the field 22,300 is somewhat low; but this may be explained by the fact that this measurement was obtained by adjusting the magnetic field until the right-hand component of the left-hand order in the eyepiece was superposed on the left-hand component of the right-hand order, an adjustment which it is somewhat difficult to make accurately.

The values given above are not accurate to more than 2 per cent.

It will be of interest to calculate the value of  $e/m$  from Larmor's equation (1), especially for the two yellow lines of mercury, since these are produced by relatively simple ionic movements. We have

$$n_1 - n_2 = \frac{eH}{2\pi mv^2},$$

where  $e$  is the charge on an ion of mass  $m$ ,

$H$  is the intensity of the magnetic field,

$v$  the velocity of light in air,

$n_1$  and  $n_2$  the frequencies of the outer components of the triplet;

hence  $\frac{v\delta\lambda}{\lambda^2} = \frac{eH}{2\pi mv^2} = \frac{eH}{2\pi m}$  in electromagnetic units.

For

$$\lambda = 5790, \quad e/m = 17 \cdot 2 \times 10^6,$$

$$\lambda = 5758, \quad e/m = 18 \cdot 9 \times 10^6,$$

$$\lambda = 5460, \quad e/m = 20 \cdot 5 \times 10^6,$$

$$\lambda = 4358, \quad e/m = 28 \cdot 0 \times 10^6,$$

For the blue and green lines, these values are calculated from the values of  $\delta\lambda_2$ ; i.e. the mean dispersion between the outer components of what was, under a weak field, a triplet.

There is one point of interest with reference to the blue and green lines which may be further noticed. The value of  $\delta\lambda/\lambda^2 H$  with the green line, is the same, both for the components of the inner triplet and for the components of the doublet into which the outer lines split. In the blue line (4358) the value of  $\delta\lambda/\lambda^2 H$  for the components of the inner doublet

is, within limits of experimental error, double that of the value of the same quantity for the components of the outer lines, and the value of  $\delta\lambda/\lambda^2 H$  for both the blue and green lines is the same, within limits of experimental error.

Whether this connexion holds good for other compound lines is a question which requires careful investigation, and on which further experiments are being made.

In working with this instrument, it was found that the yellow and green lines were far easier to examine than the blue, on account of the diminution in the dispersive power of the instrument for the longer wave-lengths. Using this grating for ultra-violet light, it would be extremely difficult to try and separate the components due to the central order, and those due to the other orders; even with the line (4358) it was some time before the splitting of the outer components became at all obvious; and seeing that what has been called the constant ( $k_1$ ) of the instrument diminishes approximately as the square of the wave-length, it is quite likely that with lines nearer the ultra-violet, components due to the fifth and sixth orders away might appear in the field. The constant ( $k_2$ ) also diminishes with shorter wave-lengths.

In order, therefore, to make this valuable instrument more serviceable for this class of work, attention should be directed to the increase of the constant without too much diminution of the resolving power. As suggested by Michelson, this might be done by surrounding the instrument, say, with water. This, however, would reduce the resolving power to only one third of its original value. A better suggestion is that of using thinner plates for the instrument and more of them. The plates might with advantage be made, say 4 mm. thick with, say, thirty plates and .5 mm. steps, or even .25 mm. steps. This would, we believe, make a more useful instrument for this work than one consisting of thirty 8 mm. plates, though theoretically the resolving-power is only half what it would be in the latter case. There is, of course, no doubt that this instrument forms a most valuable addition to the apparatus available for work on the Zeeman effect.

Blythswood Laboratory,  
Renfrew, N.B.

XXXV. On Mr. Morris-Airey's Paper on Electrolytic  
Conduction in Gases.

To the Editors of the Philosophical Magazine.

Cambridge,  
March 2, 1900.

GENTLEMEN,—

M R. MORRIS-AIREY, in his paper in the Philosophical Magazine for March, describes an experiment which shows that when the electric discharge passes through a mixture of hydrogen and chlorine, though the chlorine lines are bright at the anode and faint at the cathode, there is a considerable quantity of chlorine in the half of the discharge-tube next the cathode. From this he concludes that there is no appreciable electrolytic transport of the chlorine through the hydrogen. I do not think this conclusion can legitimately be drawn from his experiments. It is evident, that if the chlorine is transported to the anode, the increase in the partial pressure of the chlorine in this region will cause a diffusion of chlorine towards the cathode, and the steady state will be reached when the backward flow due to diffusion is equal to the forward flow due to electrolytic conduction, so that an electrolytic flow is consistent with the existence of a considerable amount of chlorine throughout the tube, and this amount will be relatively more important as the amount of chlorine in the tube increases. Mr. Morris-Airey worked with large quantities of chlorine amounting to 6 or 7 per cent. of the total amount of gas. In my experiments (Proc. Roy. Soc. lviii. p. 244) a very small quantity of chlorine was introduced into a tube filled with hydrogen, and the effects observed were not merely the presence of the chlorine lines at the anode and their absence at the cathode when the current was steady, but it was found that on the reversal of the current, so that the old anode became a cathode, the chlorine lines at first flashed out brightly at the new *cathode* and were faint at the anode, then there was a short interval during which they were faint at both electrodes, and, finally, they became bright at the new anode and invisible at the cathode. This seems very complete proof of the transport.

Yours very truly,  
J. J. THOMSON.

*XXXVI. Heat of Combination of Metals in the Formation of Alloys.* By ALEXANDER GALT, D.Sc., F.R.S.E.\*

IN a lecture delivered at the Royal Institution, London, in 1883, Lord Kelvin † refers to the want of knowledge regarding the heat of combination of zinc and copper. Two or three years ago few experiments and no measurements had been made to determine the heat of combination of these or of other pairs of solid metals. Not only in connexion with the theory of contact electricity in particular, but generally in respect to chemical affinities, it is important that we should have some knowledge in regard to this question ; and at Lord Kelvin's request I have since made an experimental investigation on the heat of combination of pairs of solid metals, particularly zinc and copper.

The results obtained have been communicated from time to time to the Royal Society of Edinburgh ‡ and the British Association for the Advancement of Science §. The British Association in 1898 granted £20 in aid of the further prosecution of the work.

The method of procedure was to dissolve a known weight of an alloy of two metals, and also under similar conditions the same weight of a mixture of the metals which are present in the alloy, the proportions taken being the same as those known to be in the alloy, and noting the initial and final temperature in each case. The heat of combination of the metals in the alloy may be estimated after noting the difference between the heats of solution in the two cases.

Messrs. Johnson, Matthey, & Co., of London, kindly made for me and analysed twenty-two different alloys of practically pure zinc and copper, whose composition varied from 5 to 90 per cent. of copper ; and they also supplied separate specimens of zinc and copper similar to those used in making the alloys. To facilitate solution the metals and alloys were first reduced to powder by filing with a fine file. The method of experimenting finally adopted was carried out in detail as follows :—One end of a short length of closed thin glass tubing was sealed to the top of a very small glass globe (see fig. 1). Near the point of attachment there were, on opposite

\* Communicated by Lord Kelvin.

† ‘Popular Lectures and Addresses,’ vol. i., “The Size of Atoms,” pp. 160–166.

‡ Proc. Roy. Soc. Edinb. 1898, pp. 137–149 ; 1899, pp. 619–621.

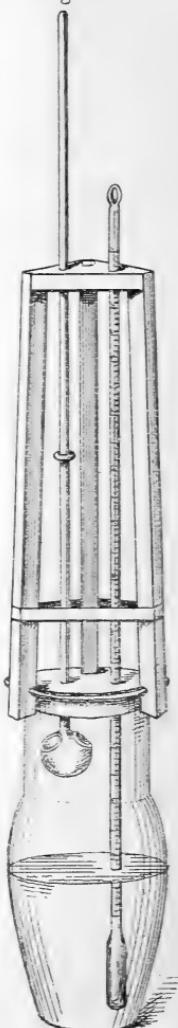
§ British Association Report 1898, pp. 787–788 ; 1899, pp. 246–249.

sides, two oval-shaped openings into the globe. The glass tube was free to move up and down a certain distance through one of two holes bored in a short common cork, specially selected. Particular care being taken to see that the globe was clean and dry, it was drawn down from the cork about 6 centims. and the cork was then fixed in a clamp. The filings (.5 gramme was the quantity generally used in the experiments) were then most carefully inserted into the bottom of the globe through one of the openings, and the globe was then drawn up close to the cork. Through the other hole in the cork a thin short-range thermometer, whose marked divisions correspond to  $0\cdot05^{\circ}$  C., was passed. The cork, carrying the globe and attached tube and the thermometer, was then carefully fixed in the neck of a small flask of thin glass containing a definite quantity of nitric acid of density 1.360 at  $15^{\circ}$  C. To avoid possible heating effects from the hand the rim of the flask was not held by the fingers; instead the rim was placed in a slit made near the bottom of each hinged limb of a small wooden tripod 4 or 5 inches long, a rubber band round this part tightening the grip.

Holding the flask by the top of the tripod, it was gently shaken so as to give the acid a rotating motion; in this way the flask and acid soon attained a uniform and steady temperature which was usually about that of the room, and it was carefully noted. The globe containing the filings was now plunged to near the bottom of the flask by quickly pushing down the glass tube to which it was attached, the downward movement being arrested by the knob on the tube.

If the method of pouring the acid on the filings or of dropping the filings into the acid had been adopted, a violent action would have occurred, and it would not have been possible to prevent the loss of heat due to escape of fumes. But the plan adopted effectually got rid of this difficulty by the almost instantaneous projection of the globe containing the filings to the bottom of the acid\*. It was interesting to

Fig. 1.



\* Andrews, 'Scientific Papers,' p. 214:—"Every chemist is familiar

watch the scouring effect in the globe due to the chemical action ; the filings were almost instantly expelled from it through the apertures by reason of the rapid evolution of gas. But in the cases of a few of the alloys and mixtures containing large percentages of copper this effect was only partial, and a considerable proportion of the powder remained in the bulb with the result that solution was much delayed. In these instances the bulb was replaced by a tiny glass basket suspended from a spiral hook formed at the bottom of the glass tube, so that when the basket containing the filings was driven to the bottom of the acid the basket was overturned and the filings scattered over the bottom of the flask.

When solution was started the flask was quickly inserted into a large cylindrical metal can through an aperture in the cover. The can had a water-jacket round the sides and bottom, and the contained air could be kept at a practically constant temperature, which was a fraction of a degree centigrade below the maximum which would be attained by the solution, by heating the water in the jacket by means of a bunsen-burner placed below the can. The temperature of the contained air was read by a sensitive thermometer suspended in the can, the bulb of the thermometer and the bottom of the flask being close together near the centre of the can.

Solution was generally effected in 55 to 60 seconds, and while it was going on the flask was shaken so as to give a rotatory motion to the acid. Complete solution and maximum temperature were nearly coincident in time.

Each experiment was repeated from three to six times until consistent results for the heat of solution in each case were obtained, and the mean of these was taken. In each case of solution the nitrous products remained in the liquid, the flask in which solution took place being kept gas-tight by the cork.

The total weight of the whole apparatus—flask, cork, thermometer, and sealed glass tube with attached globe or basket —was 42 grammes, and the water equivalent was found to be 5·7 grammes. The specific heat of the nitric acid used was repeatedly determined, and the mean of several values was ·658. The specific heat of the metal used is negligible and was not taken into account.

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with the violent action of nitric acid on zinc and copper, and the abundant evolution of gas which accompanies it. But the facility with which the gases may be condensed by the acid solution is probably not so generally known, and when the experiment is made for the first time it cannot fail to excite surprise."

The absolute amount of heat evolved in dissolving 1 grammé of metal is calculated from the following formula:—

$$H = t \{ (v\rho s) + c \},$$

where  $t$  = increase of temperature, in centigrade degrees, of the acid used per grammé of metal dissolved,  
 $v$  = volume of the acid in cubic centimetres,  
 $\rho$  = density of the acid,  
 $s$  = specific heat of the acid,  
 $c$  = water equivalent of the apparatus.

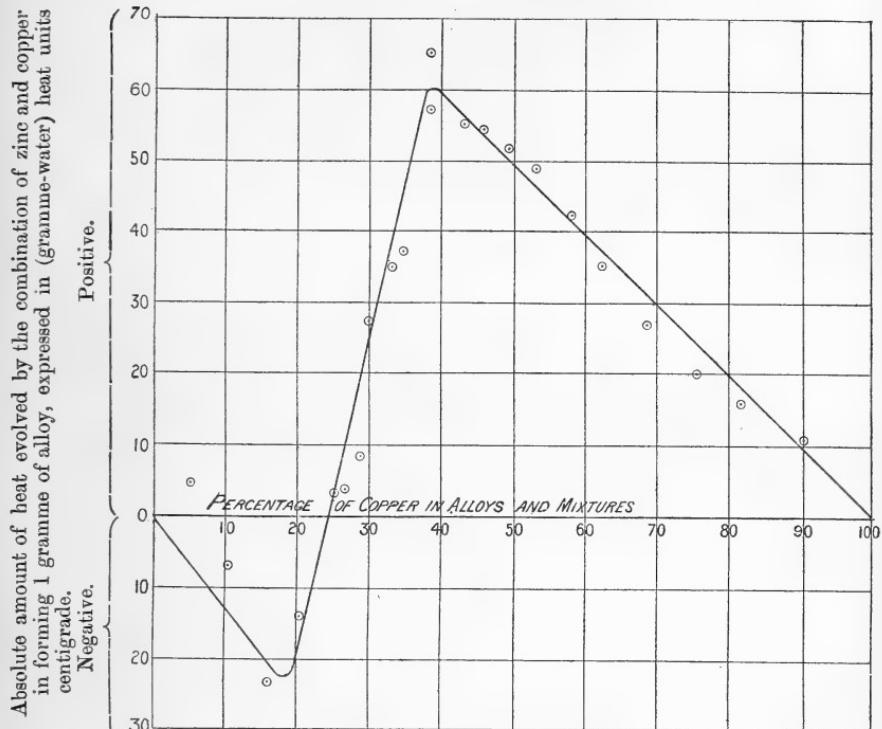
The accompanying tabular statement (p. 410) shows the quantitative composition of each of the twenty-two alloys of zinc and copper, the quantities of metal and acid used in each set of experiments, the mean increase of temperature of the acid per grammé of metal dissolved, and the absolute amount of heat evolved in dissolving this weight of alloy and mixture.

Assuming the products of solution of each mixture and its corresponding alloy to be the same\*, the difference between the absolute amount of heat of solution of 1 grammé of each mixture and its corresponding alloy indicates the heat of combination of the metals in forming 1 grammé of alloy. These differences are shown in fig. 2, and they indicate that the heat of combination is at first negative, this negative value reaching a maximum when the alloy contains about 16 per cent. of copper. With greater percentages of copper the negative value of the heat of combination rapidly falls to zero, and then becomes positive. The maximum positive value is very soon reached at about 38 per cent. copper, which is near the formula  $Cu_2Zn_3$ . Beyond this point the heat of combination gradually becomes less, until at 90 per cent. copper it almost vanishes.

Further experiments were made with the alloy which gave the greatest negative heat of combination, and also with the alloy which gave the greatest positive value. In each case when the solution of the mixture and that of the alloy had reached room-temperature, they were mixed together; but no appreciable change of temperature was observed.

\* Chemical investigation would be necessary to test the truth of this assumption. It is possible that there may be differences in the chemical products; but it seems scarcely probable that such differences, if they exist, can largely modify the thermal results which are the subject of the present communication.

Fig. 2.—Heat of Combination of Copper-Zinc Alloys.



Messrs. Johnson, Matthey, & Co. also made and analysed for me five different alloys of silver and copper, containing respectively 64·7, 44·6, 22·7, 15·3, 10·4 per cent. of copper. A considerable number of preliminary experiments have been made with these with the view of determining their heat of combination. The method of procedure was somewhat similar to that described for the zinc-copper experiments. The solvent was again nitric acid, but of lower density than that used in the zinc-copper experiments. To still further facilitate solution, which was slow, the metals and alloys had first to be reduced to exceedingly fine filings by the laborious process of filing down with a very fine file. The results indicate little or no heat of combination.

No. of Alloy.	Percentage Composition of Alloy.	Weight of Metal dissolved in each Experiment.	Quantity of Acid used in each Experiment.	Mean Increase of Temperature of Acid <i>per gramme</i> of Metal dissolved, expressed in degrees centigrade.			Mixture.	Alloy.	Difference.	Absolute Amount of Heat evolved in dissolving 1 gramme of Metal, expressed in (gramme-water) heat units centigrade.	This difference represents the Absolute Amount of Heat evolved by the Combination of Metals in forming 1 gramme of Alloy.
				Copper.	Zinc.	Difference.					
1	5.00	95.00	.4	14.52	14.47	+0.05	138.5	138.0	+4.7	1380.3	+4.7
2	10.50	89.50	.4	14.77	14.85	-0.08	1340	1346.8	-6.8	-23.0	-23.0
3	16.00	84.00	.4	16.65	16.55	-0.30	1287	1310	-23.0	-14.0	-14.0
4	20.50	79.50	.4	15.23	15.40	-0.17	1244	1258	-3.5	1198.5	+3.5
A	25.14	74.86	.5	90	13.94	13.90	1202	1172.5	+38	1176.3	+38
5	26.50	73.50	.5	100	12.54	12.50	10.04	1194	+86	1185.4	+86
L	28.75	71.25	.5	90	13.84	13.74	+0.10	1171	+27.0	1144	+27.0
M	30.00	70.00	.5	90	13.58	13.26	+0.32	1171	+35.0	1094	+35.0
N	33.00	67.00	.5	80	14.60	14.14	+0.46	1129	+37.0	1123	+37.0
O	34.50	65.50	.5	80	14.52	14.04	+0.48	1086	+65.0	1034	+65.0
6	38.00	62.00	.5	90	12.74	11.98	+0.76	1093	+57.0	1035	+57.0
B	38.38	61.62	.5	90	12.66	12.00	+0.66	1092	+55.0	1011	+55.0
P	43.00	57.00	.5	90	12.36	11.72	+0.64	1066	+54.0	993	+54.0
7	45.50	54.50	.5	80	13.54	12.84	+0.70	1047	+51.0	1016	+51.0
C	49.10	50.90	.5	80	13.14	12.48	+0.66	988.8	+49.0	939.8	+49.0
Q	52.50	47.50	.5	75	13.58	12.90	+0.68	952.8	+42.0	910.8	+42.0
R	58.00	42.00	.5	70	13.94	13.32	+0.62	915.8	+35.0	880.8	+35.0
D	62.27	37.73	.5	70	13.40	12.88	+0.52	866.8	+27.0	839.8	+27.0
S	69.00	31.00	.5	70	12.68	12.28	+0.40	807.9	+20.0	787.9	+20.0
E	75.225	24.775	.5	70	11.82	11.52	+0.30	762.6	+16.0	746.6	+16.0
T	81.50	18.50	.5	70	11.16	10.92	+0.24	684.5	+11.0	695.5	+11.0
V	90.25	9.75	.5	70	10.02	+0.16					

## XXXVII. Notices respecting New Books.

*An Introduction to the Differential and Integral Calculus and Differential Equations.* By F. GLANVILLE TAYLOR, M.A. (Longmans, 1899, pp. xxiv+568.)

THIS is an excellent text-book. At this time of day much novelty is not to be looked for, and indeed, considering the Author's object, novelty would militate against utility. His aim has been to present each subject in a clear and simple manner, "rather than to introduce any special novelties." In our opinion, after a careful perusal, he has certainly succeeded in investing the subject with interest. All the best authorities have evidently been consulted, and the portions most suitable for students thoroughly assimilated and reproduced in a clear and lucid manner.

The Differential and Integral Calculus are treated fully, *i.e.* to the extent suitable for elementary readers, and there is, as has lately been the case in recent similar works, a short but sufficient, for ordinary purposes, account of Elementary Differential Equations. There is a very large collection of examples and many useful ones have been clearly worked out, in many cases two, or more, alternative proofs have been given. The figures have been well drawn and the printing is very clear. The examples are freely distributed throughout the text, and answers immediately follow these exercises. We have noted very few clerical slips. P. 26, Question 7 and the Answer do not agree: p. 27, l. 2 up, for one +, read - : p. 65, l. 3 up, for M read N : p. 77, line 1, for NR read NQ : p. 100, l. 7, read "namely": p. 101, line 3, for "negative" read "positive": p. 143, it might be stated that the  $\theta$ 's (in § 155) are not the same, but general: p. 159, l. 1 up, for  $-3t^2$  read  $+3t^2$ : p. 186, D in the figure should be O: art. 272, Ex. 1 might have a reference to p. 272, Ex. 5, where the question is discussed further: p. 412, l. 9 up, for final  $m$  read  $y^{m+n+2}$ : p. 413, l. 10, read "integrable": p. 446, l. 7 up, add " $dx$ " at end: on p. 457 "s" is used in two senses, and so elsewhere: § 464, read  $\bar{x}$ ,  $\bar{y}$ , once: p. 498, l. 3, read  $Ndy$ : p. 543, l. 10, for  $D^n$  read  $D^4$ . All these errors are trifling, and the student would easily detect them. We have tested a fair number of the questions, but where there are so many it is inevitable there should be several slips, but we have not come across them. A full "Contents," two pages of "definitions of theorems in Algebra and Trigonometry," and an "Index" complete the work.

*Science Abstracts, Physics and Electrical Engineering.* Vol. II., 1899.—Issued under the direction of The Institution of Electrical Engineers and The Physical Society of London.

We are glad to record the completion of another volume of this excellent publication, which offers to English readers a trustworthy outline of nearly all the original work in physics and electrical engineering that is published from month to month, either in their own or other languages. Absolute completeness in a review of this kind is of course unattainable, and where so much is accom-

lished it is perhaps ungracious to ask for still more. We think it worth while, however, to point out that the scientific work of the Netherlands, Belgium, and Switzerland is hardly completely represented by the *Archives néerlandaises* and the three electro-technical journals included in the list of journals abstracted. No doubt much of the work published in these countries comes under review at second hand, but abstracts of abstracts are apt to be scrappy if not actually inaccurate. We think also that the 'Report of the British Association' might be put on the list of works occasionally abstracted. There is probably on an average as much matter in each volume which it is desirable to include as there is in an ordinary year's issue of the 'Automotor and Horseless Vehicle Journal' or the 'Tramway and Railway World.'

Readers of the Philosophical Magazine will naturally take more interest in the section devoted to "Physics" than in that dealing with "Electrical Engineering;" and we are glad that the attention given to the latter part does not seem in any degree to have been accompanied by slackness in regard to the former. The standard set up by the Physical Society during the three years that they issued their 'Abstracts of Physical Papers' seems to be fully maintained, and the list of papers abstracted is more complete.

We understand that arrangements have been made between the two Societies concerned in the Publication of 'Science Abstracts' whereby its continuance on the present plan is insured for at least three years. By the end of this time we may hope that the value of the work will be so widely recognized and appreciated, that there will be no difficulty of a financial kind in the way of its future prosperity.

*Le Magnétisme du Fer.* Par CH. MAURAIN. Paris: Georges Carré & C. Naud, 1899. Pp. 1–100.

The publishers are to be congratulated on the series of scientific monographs of which the little book before us is one. They are clearly printed, well illustrated, and written by authors of undoubted eminence in the subjects with which they deal. The only two defects which one cannot help noticing are the somewhat flimsy paper binding and—what is much more serious—the *absence of an index*. Surely in these days it is almost unpardonable for any writer to produce a book on a scientific subject without preparing an index for it. Apart from these blemishes, however, we have nothing but praise to bestow on the work before us, where, within the small compass of 100 pages, the author gives a very exhaustive and up-to-date, if somewhat compressed, account of the phenomena of Magnetism. The book is not intended to be an introductory text-book for beginners; indeed, the necessarily concise nature of the author's exposition renders it quite unsuitable for this purpose. But to the advanced worker, to whom it is addressed, it will prove a most useful *résumé* of the numerous recent experimental researches in the domain of Magnetism.

It is becoming increasingly more difficult to keep pace with the advancing wave of scientific research; and students of Magnetism

will feel grateful to M. Maurain for the exceedingly useful account of what has already been done in this branch of experimental science. Beginning with a general account of the phenomena of magnetic induction, the author briefly describes the various methods of measuring magnetic quantities, and the instruments used for this purpose. Next follows a detailed study of the magnetic qualities of iron and steel. This is succeeded by a chapter dealing with the vexed question of viscous hysteresis; and the next two chapters are devoted to a discussion of the dissipation of energy by hysteresis, and the effects of temperature changes. A short sketch of the theories of magnetic induction concludes this little book, which we can unhesitatingly recommend to all interested in magnetic research.

*Le Phénomène de Zeeman.* Par A. COTTON. Paris: Georges Carré & C. Naud, 1899. Pp. 1–100.

Another excellent little book belonging to the same series as that referred to in the last notice.

The steady improvement which has, since the commencement of the 19th century, been taking place in the construction of physical measuring instruments, has produced important results in enabling the physicist to study many phenomena whose very existence could not be detected by the crude apparatus at the disposal of some of the early workers in physical science. What Faraday looked for, but looked for in vain, it has been reserved for Zeeman, equipped with the wonderfully perfect instruments now available, to discover and interpret. In the little book before us, the author gives a connected account of the various phenomena directly or indirectly related to the Zeeman effect. After a brief discussion of the various forms of diffraction-gratings, the author considers how a change in the wave-length of a given radiation may be produced. Next comes a short historical account of the researches which preceded Zeeman's great discovery, and this is followed by a detailed account of the discovery itself. The remainder of the book deals with the most recent experiments bearing on this subject. Numerous references to original sources of information are given. The book will prove extremely useful to all interested in the subject with which it deals.

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### XXXVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 328.]

January 10th, 1900.—W. Whitaker, B.A., F.R.S., President,  
in the Chair.

THE following communications were read:—

1. ‘On a Particular Form of Surface, the Result of Glacial and Subaerial Erosion, seen on Loch Lochy and Elsewhere.’ By Dr. W. T. Blanford, F.R.S., Treas.G.S.

This form of surface, first noticed by the author on Lake Como, was afterwards observed in the Great Glen of Scotland and in

British Columbia. It consists of an almost even plane sloping at a moderate or high angle, and cut at intervals by small ravines or channels. The sides of the Great Glen have been planed by glacier-action to a greater extent than usual, and between Loch Lochy and Loch Oich, near Laggan, the sides of the Glen have a regular and flat slope of over  $35^{\circ}$  up to about 1000 feet above sea-level. Numerous stream-cut channels draining down this slope are, on an average, not more than 10 to 15 feet deep, but some quite exceptional examples may be 50 feet deep; these channels occupy less than a fourth of the surface. In addition there are larger glens which, although they run out into shallow ravines where they cut the sloping side of the Great Glen, are frequently 500 feet in depth among the hills. If these were ordinary stream-valleys before the Glacial Period, the cutting away of the ridges separating them to the extent of at least 250 or 300 feet must be attributed to glacial erosion on the sides of the Great Glen. The erosion of the small ravines in the glacial slope must have been effected by streams in post-Glacial times, and the measurement of their rate of erosion might be expected to throw light on the amount of time which has elapsed since the Glacial Period in this district. 'The general effect produced by the whole evidence is . . . the small amount of denudation that has taken place since the Great Ice Age, and the necessary deduction that no great period of time, measured in years, can have elapsed between the Glacial Epoch and the present day.'

2. 'On the Geology of Northern Anglesey: Part II.' By C. A. Matley, Esq., B.Sc., F.G.S.

The present paper deals in the first place with the stratigraphy of the Northern Complex. The following table shows the succession of the rocks in descending order:—

C. THE LLANDEILO STRATA.

Feet.

Cd. Black argillaceous shales .....	40, top not seen.
Cc. Ironstone, in part oolitic .....	20
Cb. Grey quartzose shales or slates, striped by thin, black laminae .....	150
Ca. 2. Pale conglomerates and grits .....	500
1. Red-purple conglomerate .....	180

B. THE LLANBADRIG SERIES, about 1000 feet or 1500; [apparent  
order:—

Bf. Quartzite.

Be. Pebby slates.

Bd. Slates with grit-and-quartzite bands.

Bc. Quartzites, shales, and some limestone (Porth Padrig, etc.).

Bb. Limestone (as at Trwyn y Parc).

Ba. Grits and slates, usually smashed to a crush-conglomerate.

A. THE GREEN SERIES.

Greenish and bluish slates (of the Northern Complex).

The rocks strike east-south-east, and dip usually at a high angle northward; a well-marked transverse fault divides the complex into western and eastern portions. The Llandeilo rocks occupy

four strips of ground in the west and three in the east, but the full succession does not occur in any one of these outcrops. The effects of compression are much marked in the purple conglomerate; the matrix is dragged out along small shear-planes, and the pebbles are stretched into phacoids, slip-faulted, and their extremities tailed out. A deceptive appearance of unconformity is also produced at the junction of grits and shales. Fossils are found in some of the rocks. The Llandeilo rocks are of importance, as they reveal the existence of at least four shattered synclines, usually faulted, and probably all overthrust on their northern boundaries.

No fossils have been found in the Llanbadrig rocks, and no more definite assertion of their age is possible than that they are pre-Llandeilo. They are newer than, and their base may be conformable with, the Green Series; but as fragments almost certainly derived from the latter series have been found in the highest zones, the relation between the two series is more likely to be that of an unconformity. The Llandeilo rocks contain fragments of limestone and pieces of quartzite; but in spite of this evidence in favour of unconformity between the Llanbadrig and Llandeilo rocks, the basal beds of the latter are found to cling closely to the highest quartzite of the Llanbadrig Group.

The quartzites are remarkable in the fact that they frequently contain patches of limestone, apparently deposited with them, and that they vary rapidly in thickness from about 30 to 200 feet at Craig Wen, where this variation is correlated by an inverse variation in the conglomerate. Although earth-movement may be partly responsible for this variation, some further explanation appears requisite, and this may possibly be furnished by erosion of the quartzite. The overthrusting force appears to have come from a direction somewhat east of north.

The igneous rocks are dealt with in two groups: those older and those newer than the earth-movement. To the former belong granite, serpentine and its associates, and basaltic dykes. In each area where they occur the serpentines are associated with masses of a peculiar purple limestone not known elsewhere; they also contain bands of ophicalcite, and schistose structures are common in the rocks. The later dykes belong to an acid and a basic set; the latter show some evidence of minor movement, such as faulting and a little shearing. The acid dykes are microgranites, granophyres, and quartz-porphries. In some cases the dykes are composite, the acid material being the older and the basic the later constituent. As a rule, the basic material invades the edge of the dyke; but in one case it has invaded the joints and cracks and caught up fragments of the acid rock.

### 3. 'The Formation of Dendrites.' By A. Octavius Watkins, Esq., A.R.S.M., F.G.S.

If two plane-surfaces be separated by a film of suitable plastic material, and one surface be rotated slowly on the other through a small arc, the plastic material collects into branching forms similar

to the structure of dendrites. The dendritic form starts from the part farthest from the axis, and the flow of material is from the smaller to the larger branches, the smaller uniting to form the larger. The author explains dendritic structure by the formation of a fissure in rock which becomes filled with a thin film of dendritic material; if the fissure is slowly widened, the dendrite starts where the widening commences, coinciding dendrites being formed on each wall. This theory is in accordance with many of the characters of dendrites, such as their method of occurrence, the nature of the material, and their uniformity in thickness.

### **XXXIX. Intelligence and Miscellaneous Articles.**

ON THE THEORY OF THE FUNCTION OF THE CONDENSER IN AN  
INDUCTION-COIL. BY DR. B. WALTER.

TWO years ago Mr. T. Mizuno published in this Magazine\* some observations on the relation connecting the spark-length in the secondary of an induction-coil with the capacity of the condenser in the primary. These observations have recently induced Mr. K. R. Johnson†, of Stockholm, to offer a theoretical explanation which, it is true, is correct, but which in my opinion presents as little novelty as the experiments themselves. In fact, some time before the appearance of Mizuno's paper, I published an article‡ containing not only an account of an identical series of experiments, but also a detailed theory of them. This article of mine has been passed over unnoticed by Mr. Johnson, although it was expressly mentioned by Mr. Mizuno, and in all probability served as a basis for the latter's experiments.

In one particular, indeed, these experiments appeared to offer a contradiction to my theory, viz., in that the capacity of the condenser for maximum spark-length was greater the greater the primary current. An explanation of this fact—first discovered by Mr. Mizuno—has not been attempted by Mr. Johnson. Now in a later communication by myself§ the fact is hinted at in the remark that with increasing current the primary spark becomes stronger—a phenomena which of course vitiates the theory. On the other hand, the relations once more recently discussed by Mr. Johnson I regarded as having been already established in my previously mentioned article.

Hamburg, State Physical Laboratory,  
March 1900.

\* T. Mizuno, Phil. Mag. xlvi. p. 447 (1898).

† K. R. Johnson, ibid. xlix. p. 216 (1900).

‡ B. Walter, Wied. Ann. lxii. p. 300 (1897); Electrical Review, xli. pp. 529 & 597 (1897).

§ B. Walter, Phil. Mag. xlvi. p. 172 (1898).

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

MAY 1900.

XL. *Note on the Theory of Solution Pressure.*  
*By S. R. MILNER, D.Sc.\**

THE theory of electrolytic solution pressures put forward by Nernst accounts for the existence of a contact difference of potential  $\Phi$  between a metal and an electrolyte containing the metal ions at an osmotic pressure  $p_1$ , of amount

$$\Phi = \frac{RT}{ne} \log \frac{P}{P_0}, \dots \dots \dots \quad (1)$$

$ne$  being the charge passing through an electrode when a gram ion of the metal is deposited electrolytically, and  $P$  a constant depending on the nature of the metal.  $P$  is generally taken as representing the actual pressure with which metallic ions tend to go into solution ; though the unsatisfactoriness of this view has been pointed out in a recent paper in this Magazine by Dr. Lehfeldt †—the values of  $P$  are in many cases so great that they cannot represent actual physical pressures.

Several thermodynamical proofs of Nernst's formula have been given ‡. It seems to me that in general in these proofs the mode of application of the second law is not perfectly stringent, in that the electrical work done in passing a unit charge through the surface is equated to the corresponding

\* Communicated by the Author.

† Phil. Mag., November 1899.

‡ Nernst, *Theoretische Chemie*, 2nd edit. pp. 665; Jahn, *Grundriss der Electrochemie*, p. 194; Leblanc, *Electrochemie*, p. 153 (Eng. trans.).

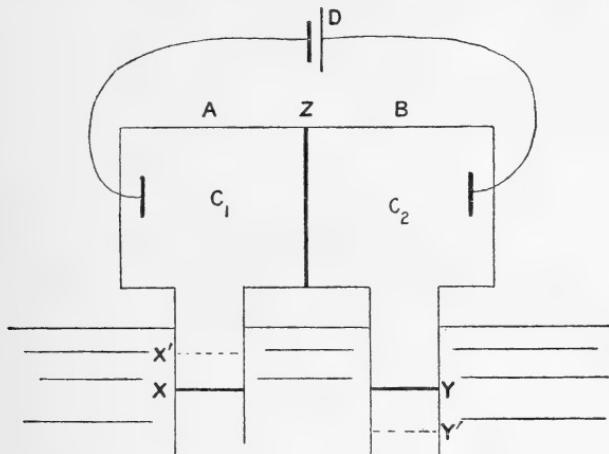
work of osmotic expansion  $\frac{1}{n\epsilon} \int_{p_1}^P p dv$  between the two pressures of the ions in the metal and the solution, without further examination. The expression for the potential step given by a cycle is, however,  $\frac{1}{n\epsilon} \int_P^{p_1} v dp$ ; and although the difference between these two results vanishes so long as the gas laws apply, it is of some importance theoretically, as for example in the application to incompletely dissociated electrolytes. A further difficulty in them is that the case is treated of a *single* electrode in a liquid, and it is impossible here to imagine reversible electrolytic solution to take place without charging up the solution, and the removal of this charge can only be brought about by the introduction of negative ions into the solution, from which process more osmotic work might theoretically be obtained. The neglect of this effect may be shown to give correct results, but the arbitrariness resulting from it makes it difficult to recognize the nature of the real assumptions on which the formula depends for its validity. For a thermodynamical proof to satisfactorily admit of this, it seems essential that the operations should be reducible to an exact cycle, in which also the *possibility* of carrying out the individual processes should be evident.

The importance of the theory is so great, in view of the remarkable way in which it has shown itself applicable to so many different phenomena in electrochemistry, that it seems advisable that the exact nature of the assumptions which underlie the validity of Nernst's formula should be recognizable as clearly as possible. The following simple derivation, by a cyclical application of the second law, which allows this recognition, may therefore not be without interest.

Take for simplicity the special case of a cell composed of silver electrodes in concentrations  $c_1$ ,  $c_2$  ( $c_1 > c_2$ ) of silver nitrate, in the vessels A and B respectively in the figure. We assume that the silver nitrate is completely dissociated, and that the ions both exert osmotic pressures ( $p_1$  in A,  $p_2$  in B) against semipermeable partitions X and Y, by the motion of which work may be done on or obtained from the cell reversibly. Electrical work may also be obtained by allowing electricity to pass round the circuit formed by balancing the cell against an accumulator D.

In order, however, to make this operation reversible, the two concentrations must be separated by some form of partition which will prevent diffusion, and yet allow the reversible passage of electricity through it. For this purpose we may

imagine a partition Z, impermeable to silver ions, but allowing the free passage of  $\text{NO}_3^-$  ions through it. A partition of this kind, though only imaginary, introduces no ideas different in principle from those connected with the actually realizable



partitions X and Y, and so cannot affect the validity of the cycle ; it would, however, have the effect on any passage of  $\text{NO}_3^-$  ions from one side to the other, of making the negative charges carried by these the sole charge transferred across it. When the cell is on open circuit the tendency of  $\text{NO}_3^-$  ions to diffuse through Z from A to B, would therefore produce at Z a potential step balancing it, the amount of which, however, may be easily calculated on the ordinary osmotic pressure theory.

The following cycle may now be carried out :—First, a charge Q is allowed to flow round the circuit, in a direction such that silver is precipitated at A, and goes into solution at B. These amounts of silver are both  $Q/ne$  gram ions,  $ne$  being the charge required to deposit 1 gram ion of the silver. At the same time  $Q/ne$  gram ions of  $\text{NO}_3^-$  pass from A to B, constituting the current through Z. Thus the volume of both the positive and negative ions in A is decreased by  $v_1 Q/ne$ ,  $v_1 (=1/c_1)$  being the volume of a gram ion of either constituent, and work is done on the cell by the motion of X to X' to the extent  $2p_1 v_1 \cdot Q/ne$ . Similarly work is obtained by the expansion of the solution in B against Y (which moves to Y') to the extent  $2p_2 v_2 \cdot Q/ne$ .

The second part consists in cutting off from the rest by a semipermeable partition the increase YY' of the silver nitrate in B, and compressing it till its concentration becomes  $c_1$ ,

when it may be transferred to A without the expenditure of further work. The work required for this compression is

$$2 \frac{Q}{n\epsilon} \int_{p_1}^{p_2} pdv.$$

Finally, the transference of the  $Q/n\epsilon$  gram ions of solid silver deposited at the A electrode, back to that in B where an equal amount was dissolved, can be accomplished without work, and the cell is by these means brought back to its initial condition. By equating the efficiency of this isothermal cycle to zero we have (reckoning work done by the cell as positive)

$$EQ + \frac{2Q}{n\epsilon} \left\{ -p_1 v_1 + p_2 v_2 - \int_{p_1}^{p_2} pdv \right\} = 0,$$

or

$$E = \frac{2}{n\epsilon} \int_{p_2}^{p_1} v dp$$

independently of the special form of the relation between  $p$  and  $v$ . The electrode in the concentration  $c_1$  is also the positive pole of the cell.

This value of the E.M.F. of course includes the potential step set up at the partition Z. The amount of this may be calculated simply, from the consideration that in the region of the partition where the concentration of the  $\text{NO}_3^-$  ions is varying from  $c_1$  to  $c_2$ , there must be no resultant motion of these in either direction. Hence the force,  $\frac{dp}{dx}\delta x$ , due to the osmotic pressure on the  $\text{NO}_3^-$  ions in a layer of unit area and thickness  $\delta x$ , must be equal and opposite to the electrostatic pull upon the same. The value of this last is the product of the potential slope  $d\phi/dx$ , and the total charge on the  $\text{NO}_3^-$  ions in the layer; that is, it is  $nec\delta x \cdot d\phi/dx$ , and acts in the opposite direction. Equating these, and integrating, we have

$$\phi = \frac{1}{n\epsilon} \int_{p_2}^{p_1} \frac{dp}{c} = \frac{1}{n\epsilon} \int_{p_2}^{p_1} v dp,$$

the potential of A being above that of B by this amount. The difference in the potential steps at the two electrodes, therefore, is  $E - \phi$ , or

$$\frac{1}{n\epsilon} \int_{p_2}^{p_1} v dp.$$

From this the value of the potential step at the single electrode in A may at once be obtained by making the concentration of the ions in B such that there is no difference of potential between the solution and the electrode in this com-

partment. Calling the osmotic pressure of the ions in B necessary to produce this  $P$ , and  $\Phi$  the excess of the potential of the electrode in A over that of the solution, we have

$$\Phi = \frac{1}{n\epsilon} \int_P^{P_1} v dp, \dots \dots \quad (2)$$

from which Nernst's formula (1) follows at once under the application of the gas law  $pv=RT$ .

In the above it has been assumed that the silver nitrate is completely dissociated. When this is not the case it is usually taken for granted that the only effective pressure in producing the potential step is that of the metallic ions. The correctness of this follows thermodynamically if the isotherm of dissociation is taken to be that given by the law of mass-action, viz.:—

$$Kc' = c^2,$$

where  $c'$  is the concentration of the undissociated, and  $c$  that of the dissociated, molecules. The expression for the E.M.F. of the cell considered above is general if it be written in the form

$$E = \int_{P_2}^{P_1} V dP,$$

where  $V$  and  $P$  represent the molecular volume and pressure of the whole salt, both the undissociated molecules and the ions. Integrating this under the conditions

$$V = \frac{1}{c' + c},$$

$$P = p' + 2p = RT(c' + 2c),$$

$$Kc' = c^2,$$

(where the 's refer to the undissociated molecules, and the unmarked letters to the ions), we get

$$E = 2 \frac{RT}{n\epsilon} \log \frac{p_1}{p_2}.$$

From this is to be subtracted the potential step  $\phi$  at Z, the value of which is  $\frac{1}{n\epsilon} \int_{P_2}^{P_1} v dp$  for the negative ions only, or  $\frac{RT}{n\epsilon} \log \frac{p_1}{p_2}$ . Hence the difference in the potential steps at the electrodes is

$$E - \phi = \frac{RT}{n\epsilon} \log \frac{p_1}{p_2}.$$

into which formula it is only the pressures of the metal *ions* at the two electrodes which enter. This result, however, does not follow except on the law of mass-action.

A further question arises as to the effect of the presence of any other salts in the solution in addition to the silver nitrate. It is clear, however, that so long as these are not reversible with respect to the electrodes, they can be cut off from exercising any pressure on the partitions X, Y, and Z by partitions impermeable to these salts, although permeable to silver nitrate, and the cycle can be carried out as before without alteration of the final result. It follows that all substances in solution which are not deposited on an electrode or otherwise removed from the solution *to an indefinite extent* by the passage of a current, however small, should produce no effect on the potential step there\*.

It will be seen from the above that Nernst's formula depends for its validity only on the osmotic pressure and dissociation theory, and on the reversibility of the electrolytic solution and deposition of the metal at the electrode. It is, as Dr. Lehfeldt pointed out †, independent of the nature of any special theory of the formation of the potential step at the electrode, so long as this admits this reversibility. On the other hand, it is very difficult to imagine a reversible equilibrium at the surface of the electrode which shall not be a dynamical one like all other chemical equilibria, that is, an equilibrium consisting in ions going into solution from the metal, and being deposited from the solution onto the metal, at equal rates; and this in itself is Nernst's theory of solution pressure. For in this case the tendency of the ions to go into solution may clearly be considered as due to a "pressure of solution" (quite independently of the assumption—necessary for the application of a cycle to a single electrode—that it can be represented by ions existing at a pressure in the metal differentiable from the rest by a semi-permeable partition). The value of this solution pressure would obviously be equal to the osmotic pressure of ions which

\* The importance of this deduction lies in the fact that it forms a general thermodynamical rule by which it may be judged whether or not the addition of any particular class of ions will affect the potential-difference at the electrode. Thus the addition of zinc nitrate to one side of a silver-nitrate concentration cell does not affect the E.M.F., as zinc is not deposited indefinitely by a current onto silver; on the other hand, the addition of mercurous nitrate produces an effect, as a current will deposit mercury from this cell. It also explains why in general the negative ion does not affect the potential step, as has been shown to be mostly the case by Neumann (*Zeit. Phys. Chem.* xiv. p. 229, 1894).

† *Loc. cit.*

had no potential-difference against the metal, *i. e.* it would be P in the equation (2),

$$\Phi = \frac{1}{n\epsilon} \int_P^{p_1} v \, dp.$$

The constant P in Nernst's equation (1) would also represent it if the gas law is applicable between the pressures  $p_1$  and P. When the value of P in this logarithmic formula, however, comes out so immense as, for instance, it does in the case of zinc ( $10^{19}$  atm.), it seems reasonable to put down the discrepancy to the failure of the gas law over the necessarily great range between  $p_1$  and P. In these cases the P of Nernst's formula could not be considered as more than a constant, having a meaning which is made evident by a comparison of equations (1) and (2). The gas law may be taken to apply between unit pressure and  $p_1$  in (2); hence P is such that  $RT \log P$  represents  $\int v \, dp$  of the ions in the solution between unit pressure and the actual electrolytic solution pressure of the metal.

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*XLI. The Relative Rates of Effusion of Argon, Helium, and some other Gases.* By F. G. DONNAN, M.A., Ph.D., Junior Fellow, Royal University of Ireland \*.

*Introduction.*

WHILE investigating argon and helium, Prof. Ramsay and Dr. Collie† have found that these gases *diffuse* through a porous plug into a vacuum with velocities which are higher, when compared with a standard gas such as oxygen, than those calculated according to the law of the inverse square root of the density. The object of the present investigation is to ascertain the relative rates of flow of these gases through a small hole in a thin-walled partition, *i. e.* their relative rates of *effusion*.

The subject of the efflux of fluids was investigated by D. Bernoulli‡. Since that time the subject has been investigated both theoretically and experimentally by numerous writers. In the present case we have only to deal with the efflux of gases. So long ago as 1804 Leslie§ suggested the determination of relative densities by this means, and in fact

\* Communicated by the Physical Society: read March 2, 1900.

† Proc. Roy. Soc. vol. Ix. p. 206.

‡ *Hydrodynamica*, 1738, Sec. 10, pr. 34, p. 124.

§ ‘Experimental Inquiry into the Nature and Propagation of Heat,’ p. 534.

described the method which was afterwards worked out by Bunsen\*. The subject was taken up by G. G. Schmidt† in 1820; and he deduced from his experiments the law of the inverse square root of the density, *i.e.* the law which was rediscovered by Graham. The subject was then treated in a masterly fashion by de Saint-Venant and Wantzel‡. They obtained the equation for the adiabatic efflux of an ideal gas on the assumption § that the pressure at the *vena contracta* is equal to the external pressure; and they likewise observed that this equation leads to absurd results when the external pressure becomes zero. Their experiments showed the efflux to be independent of the external pressure when the latter is less than about one-half the pressure in the gas-reservoir; and they suggest empirical formulæ for dealing with this case. About this time occur the classical experimental researches of Graham ||. His experiments were conducted with minute holes in very thin-walled partitions; and he coined the word effusion to denote the efflux in this case. It must be observed, however, that so long as the apertures are not comparable with molecular dimensions, the phenomenon of effusion is simply that of efflux on a small scale. The important point is that the diameter of the hole should be sufficiently large, when compared with the thickness of the partition, to render the effects due to viscosity negligibly small. Graham's experiments established the law of the inverse square root of the density ¶. Hydrogen, however, showed a marked deviation, which was rightly attributed by Graham to the effect of viscosity being more marked in this case owing to the lightness of the gas. The efflux of gases was investigated by Weisbach\*\*, and by Thomson and Joule ††; but the theory was not advanced beyond the point to which it been carried by Saint-Venant and Wantzel. In 1886 the adiabatic theory of efflux was subjected to an elaborate experimental investigation by Hirn ‡‡, who rediscovered §§ the phenomenon

\* *Gasometrische Methoden*, Braunschweig, 1857, p. 128 *et seq.*

† Gilb. *Ann. Bd. lxvi.* p. 39 (1820).

‡ *Journ. de l'Ecole Polyt.* tom. xvi. cah. 27, p. 85 (1839).

§ Navier, "Mémoires sur l'Écoulement des Fluides Élastiques," tome viii. de l'*Académie des Sciences*, Juin 1829.

|| Phil. Trans. iv. p. 573 (1846).

¶ Many of Graham's results show that the "law" is subject to considerable deviations.

\*\* *Experimental Hydraulik*, 1855, p. 184 *et seq.*

†† Proc. Roy. Soc. 1856, p. 178,

‡‡ *Ann. de Chim. et de Phys.* sér. 6, tom. vii. p. 289 (1886).

§§ It is remarkable how often this phenomenon has been rediscovered. Thus it was observed by Graham, Hirn, Napier (Engineer, 1867), Wilde (Phil. Mag. 1886).

observed by Saint-Venant and Wantzel, and came to the conclusion that the theory was incorrect. In the same year, however, Hirn's experimental results were very fully recalculated by Hugoniot\*, who showed that they were not in discord with the theory when the latter was extended in some important respects. The experiments of Wilde led Osborne Reynolds † to reinvestigate the theory, and he arrived, practically simultaneously with Hugoniot, at the same important extension of the theory. Quite recently the efflux of gases has been the subject of an elaborate memoir by Parenty ‡, who rejects the formulæ given by the adiabatic theory, and proposes other formulæ in their stead. Finally, the secondary phenomena in the jet have been investigated by E. Mach and Salcher, L. Mach, R. Emden, and others §.

### Theory.

- Assuming (1) That viscosity effects are eliminated,
- (2) That the ideal gas laws hold,
- (3) That the outflow is adiabatic,
- (4) That the motion is steady,

the theory given by Saint-Venant and Wantzel, and extended by Hugoniot and Osborne Reynolds, leads to the formula :—

$$\text{Mass-efflux} = S' p_0 \left( \frac{p_1}{p_0} \right)^{\frac{1}{\gamma}} \sqrt{\frac{2\gamma}{\gamma-1}} \frac{1}{RT} \left[ 1 - \left( \frac{p_1}{p_0} \right)^{\frac{\gamma-1}{\gamma}} \right],$$

where  $S'$  = area of *vena contracta*,

$p_0$  = pressure inside gas-reservoir,

$p_1$  = external pressure,

$\gamma$  = ratio of two principal specific heats,

$T$  = temperature of quiescent gas in reservoir,

provided the external pressure is greater than a certain fraction of the internal pressure in the gas-reservoir.

I have not carried out experiments under the conditions required by this formula for several reasons :—(1) The formula does not lead to simple comparative results for two gases possessing *different* values for  $\gamma$ . (2) The efflux in this case is slower, and therefore less likely to be adiabatic. (3) The efflux is dependent on the back pressure, which introduces an additional variable factor in comparative experiments. If,

\* C. R. 1886, *passim*; Ann. de Chim. et de Phys. Nov. 1886.

† Phil. Mag., March 1886.

‡ Ann. de Chim. et de Phys. viii. pp. 1–79 (1896), xii. pp. 289–373 (1897).

§ Wied. Ann. lxix. 1, pp. 264–289 (1899), where Emden gives references to the previous literature.

however,  $p_1 < \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}} p_0$ , then the theory leads to the formula

$$\text{Mass-efflux} = S' \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{2(\gamma-1)}} \sqrt{\gamma p_0 \rho_0},$$

where  $\rho_0$  = density of quiescent gas in reservoir.

Hugoniot's recalculations of Hirn's results show that  $S'$ , the area of the vena contracta, must be taken as a function of the pressure, unless the orifice in the thin plate be provided with a conical or conico-cylindrical nozzle. In the following experiments  $S'$  is therefore taken as a function of the pressure; but it is assumed that this function does not vary with the nature of the gas which is effusing.

In the paper referred to above Parenty has succeeded in representing Hirn's results by means of the empirical formula

$$V_0 = \sqrt{2a} \cdot mS \sqrt{\frac{2g}{\rho_0} \left[ p_0 - p_1 - \frac{m}{2ap_0} (p_0 - p_1)^2 \right]},$$

where  $S$  = area of orifice,

$m$  = a coefficient varying with the nature of the orifice or nozzle,

$2a$  = a constant varying with the nature of the gas,

$V_0$  = volume-efflux.

If we imagine  $V_0$  plotted against  $p_1$  as the latter decreases from  $p_1 = p_0$  to  $p_1 = 0$  ( $p_0$  remaining constant), it will be observed that  $V_0$  becomes a maximum for  $1 - \frac{p_1}{p_0} = \frac{a}{m}$ , and that the maximum value is given by

$$(V_0)_{\max.} = aS \sqrt{2gm \frac{p_0}{\rho_0}}.$$

This value is independent of  $p_1$ . Parenty regards the efflux as "regulating itself" when  $p_1$  falls to the value  $\left(1 - \frac{a}{m}\right)p_0$ , and becoming constant and equal to the above value. The critical value of  $p_1$  on the adiabatic theory is given by

$$1 - \frac{p_1}{p_0} = 1 - \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma}{\gamma-1}}.$$

In Parenty's formula the critical value of  $p_1$  corresponds to

$$\left(1 - \frac{p_1}{p_0}\right) = \frac{a}{m}.$$

Hence, to make both theories agree in the critical value of  $p_1$ , we have

$$a = m \left\{ 1 - \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma}{\gamma-1}} \right\}.$$

According to Parenty, therefore, we have, for the volume-efflux in the region where  $p_1 <$  the critical value, the formula

$$V_0 = mS \left[ 1 - \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma}{\gamma-1}} \right] \sqrt{\frac{2gm p_0}{\rho_0}}.$$

It remains now to consider the application of these results to the conditions under which the following experiments were carried out. The first remark to make is that  $p_0$  was not kept constant, but decreased considerably during the course of an experiment. If, however, we neglect acceleration-terms we may consider the equations as giving the *instantaneous* efflux at any moment, and integrate between the limits of pressure corresponding to any actual experiment. Secondly, the dimensions of the apparatus were so chosen that the back-pressure  $p_1$  in the receiver (which was initially vacuous) never attained its critical value, which is about one-half of  $p_0$ . Accordingly we have to apply either the equation

$$\text{Mass-efflux} = xS \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{2(\gamma-1)}} \sqrt{\gamma p_0 \rho_0} \quad (\text{Hugoniot-Reynolds}),$$

or the equation

$$\text{Mass-efflux} = mS \left[ 1 - \left( \frac{2}{\gamma+1} \right)^{\frac{\gamma}{\gamma-1}} \right] \sqrt{2gm p_0 \rho_0} \quad (\text{Parenty}).$$

The progress of the effusion was determined by means of a closed mercury barometer-gauge attached to the reservoir out of which the gas was effusing; so that the volume of the gas-reservoir was not constant, but a *function* of the pressure  $p_0$  of the gas in the reservoir at any moment. Call this  $\phi(p_0)$ . Accordingly the mass-efflux is given by

$$-\frac{dM}{dt} = -\frac{1}{RT} (\phi + p_0 \phi') \frac{dp_0}{dt}.$$

If we put

$$\left( \frac{2}{\gamma+1} \right)^{\frac{\gamma+1}{2(\gamma-1)}} \gamma^{\frac{1}{2}} = f(\gamma),$$

we can also write, using the adiabatic theory,

$$-\frac{dM}{dt} = Sf(\gamma) \frac{x\rho_0}{\sqrt{RT}},$$

where  $x$  is a function of  $p_0$ . Equating these values and integrating, we obtain for the time  $t$ , during which the pressure in the reservoir sinks from  $p_0'$  to  $p_0''$ , the equation

$$t = \frac{1}{Sf(\gamma)\sqrt{RT}} \int_{p_0''}^{p_0'} \frac{\phi + p_0\phi'}{xp_0} dp_0.$$

If now we measure the times  $t_1$  and  $t_2$  for two different gases, in the same apparatus, at the same temperature, and between exactly the same limits of pressure, we obtain the very simple formula

$$\frac{t_1}{t_2} = \frac{f(\gamma_2)}{f(\gamma_1)} \sqrt{\frac{\rho_1}{\rho_2}}.$$

Employing Parenty's elliptical formula, we obtain

$$\frac{t_1}{t_2} = \frac{\phi(\gamma_2)}{\phi(\gamma_1)} \sqrt{\frac{\rho_1}{\rho_2}},$$

where

$$\phi(\gamma) = 1 - \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma}{\gamma - 1}}.$$

Suppose now that  $\gamma_1 = 1.408$  and  $\gamma_2 = 1.67$ . Then we obtain

$$\frac{t_1}{t_2} = 1.06 \sqrt{\frac{\rho_1}{\rho_2}} \quad (\text{Hugoniot-Reynolds}),$$

$$\frac{t_1}{t_2} = 1.084 \sqrt{\frac{\rho_1}{\rho_2}} \quad (\text{Parenty}).$$

These results indicate a marked deviation from the simple "isothermal" formula  $\frac{t_1}{t_2} = \sqrt{\frac{\rho_1}{\rho_2}}$  in cases where two gases are compared which possess very different values for  $\gamma$ . It accordingly becomes a matter of great interest to measure the relative effusion-rates of two such gases as argon and oxygen, which approximate very closely in their behaviour at moderate temperatures and pressures to the ideal gas and yet possess very different values of  $\gamma$ . The theory indicates that argon ought to effuse, when compared with oxygen, considerably faster than would be calculated from the densities alone.

#### *Method of Measurement and Description of Apparatus.*

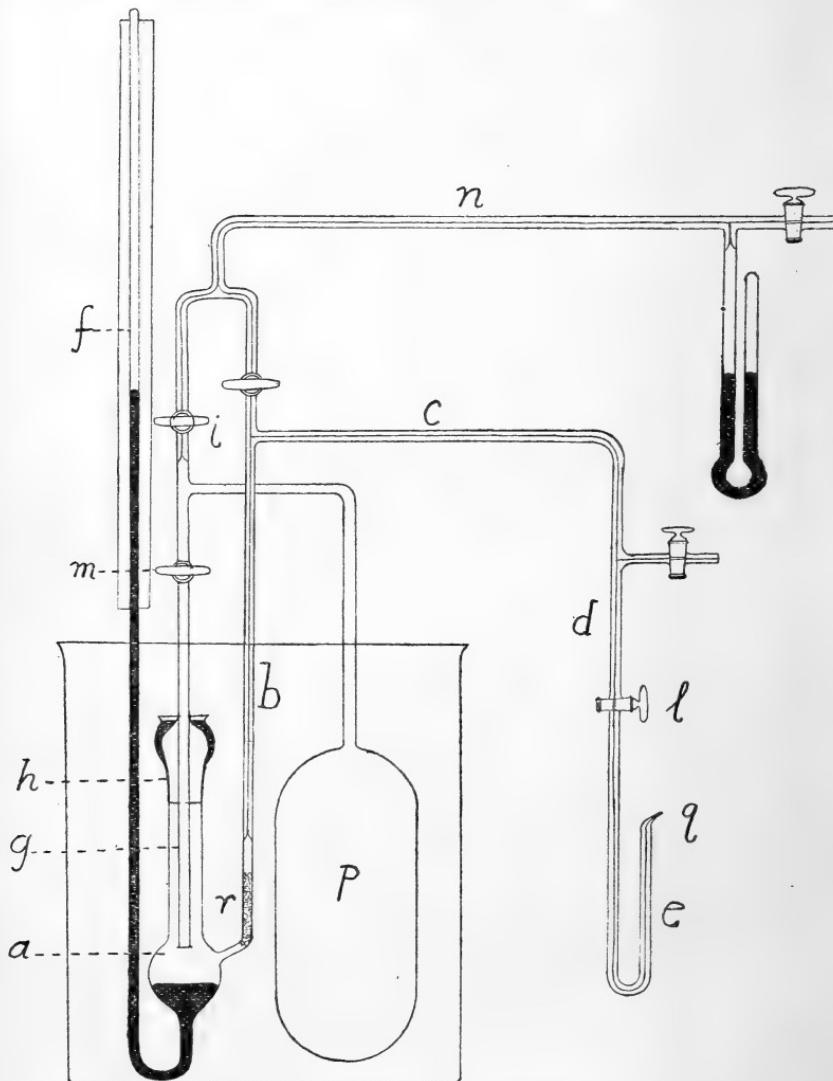
It will be seen that the theory sketched in the foregoing section only leads to simple comparison-formulae for the case of effusion in which the back-pressure is small in comparison with the pressure in the gas-reservoir. The following expe-

riments were made with an initial pressure in the gas-reservoir which was about 700 mm. in one series and about 500 mm. in the others, the back-pressure rising from zero to 60 and 47.5 mm. respectively. The principal condition was, however, that the apparatus should be such as to admit of measurements being made with small quantities (20–30 c.c.) of the rarer gases. It was necessary, therefore, to employ very small apertures in order to reduce the unavoidable error in the time-measurement\* to a sufficiently small percentage. There was a limit placed to the thickness of the partition, seeing that it had to withstand pressures approaching that of an atmosphere without collapsing, and so the conditions imposed tended rather in the direction of viscosity-effects. As will be seen in the sequel, such effects made themselves apparent. They could doubtless have been avoided by the employment of large quantities of gas and much larger apertures, but that was not possible in the present case. The apparatus employed is shown in the figure: *a* is the gas-reservoir, the gas being introduced through the capillary tubing *bcd* by means of the gas-syphon *e*. The pressure was read off in the closed barometer-gauge *f* by means of a mirror-glass scale. The effusion-plug, or partition containing the effusion-aperture, was placed at or near the lower extremity of the glass tube *g*; *h* represents a ground-glass joint with external mercury seal. During an experiment, the taps *i*, *j*, *k*, and *l* being closed and *m* open, the gas passed from the reservoir *a* into the vacuous receiver *p* through the narrow aperture in the effusion-plug. The tube *n* led to a Töpler pump, which served to evacuate the apparatus and to collect the gas again at the conclusion of an experiment. Both gas-reservoir and receiver were kept at a constant temperature by being immersed in a very large beaker of water. The temperature of the water was maintained uniform and constant by means of a stirrer with horizontal screw-shaped blades driven by a Heinrici hot-air motor and an Ostwald temperature-regulator filled with toluene.

In order to make a measurement with the apparatus, the mode of procedure was as follows:—The end *q* of the bent capillary tube was drawn off to a fine point and sealed. The taps *i*, *j*, *l*, and *m* were opened and the apparatus exhausted. These taps were then closed, and the tube containing the gas over mercury brought over the sealed point *q* by raising and lowering the mercury trough. The drawn-out end, which had been previously weakened by a file-scratch, was now broken by pressing the top of the tube against it, and the

\* The time was measured by a stop-watch marking fifths of a second.

gas admitted to the reservoir by opening the tap  $l$ . On its way thither it was filtered through the cotton-wool plug  $r$ . The gas was allowed to enter until the mercury in the gauge rose to a certain fixed scale-division  $n_1$ . It was easy to adjust



this accurately, provided the capillary had been drawn out fine enough ; and in any case small inaccuracies in this adjustment are absolutely without effect on the measurements, as is foreseen from the theory and as will be confirmed later on. The

tap *l* having been closed, the effusion was started by opening the tap *m* and a stop-watch set in motion as soon as the mercury meniscus sank to a certain scale-division *n*<sub>2</sub> a little below *n*<sub>1</sub>. A smooth and easy motion of the falling mercury meniscus was secured by having a small quantity of glycerine in the gauge, *i. e.* just sufficient to lubricate the glass wall but not enough to collect over the mercury. The watch was stopped as soon as the meniscus reached a third fixed division, *n*<sub>3</sub>. Proceeding in this way with each of the gases to be compared, it will be seen that the times of effusion are measured between exactly the same limits of pressure. The pressure in the receiver at the end of the effusion was measured roughly by opening *i* and reading the closed gauge *S*. In order to make two consecutive measurements, it was only necessary to open *i*, pump out the receiver *p*, close *i*, and readjust the pressure in the reservoir to *n*<sub>1</sub> by admitting more gas.

#### *Experimental Results.*

Besides argon and helium the following gases were investigated :—Hydrogen, oxygen, carbon monoxide, nitrogen, carbon dioxide, and cyanogen. The methods employed in their preparation may be briefly indicated here.

*Oxygen.*—By heating KMnO<sub>4</sub>. Dried by P<sub>2</sub>O<sub>5</sub>.

*Hydrogen.*—By heating palladium-hydrogen in vacuo.

Dried by P<sub>2</sub>O<sub>5</sub>.

*Nitrogen.*—Prepared in vacuo from sodium hypobromite solution and ammonium chloride. Passed through powdered NaOH, and dried by P<sub>2</sub>O<sub>5</sub>.

*Carbon monoxide.*—Prepared directly over mercury by addition of concentrated formic acid to excess of concentrated sulphuric acid.

*Carbon dioxide.*—By heating NaHCO<sub>3</sub> in vacuo. Dried by CaCl<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>.

*Cyanogen.*—Prepared by heating Hg(CN)<sub>2</sub> in vacuo and dried by P<sub>2</sub>O<sub>5</sub>. Purified by freezing out in bath of liquid air and pumping off any admixed nitrogen.

The first experiments were made by using very thin-walled glass bulbs in which minute holes had been pierced. This piercing was effected by employing the spark from a Wimshurst machine between terminals of platinum wire. When an aperture of suitable dimensions had been obtained in this way, the stem of the bulb was sealed on close to a capillary tap, and the whole then sealed into the gas-reservoir. Accordingly, in these first measurements, the effusion vessel

had a form which was somewhat different to that described previously and used in the subsequent experiments. In other respects the apparatus was the same. All the experiments were carried out at the temperature of 25° C. It is of course necessary to keep the temperature very constant during an experiment, as the apparatus acts like a gas-thermometer. The following times of effusion were observed :—

	m.	s.	m.	s.
Hydrogen . . . .	3	47·9,	3	47·8
Oxygen . . . .	12	21·3		
Carbon monoxide .	11	16·4,	11	18
Nitrogen . . . .	11	18,	11	17·8.

It is evident from the results for hydrogen and oxygen that there is a large viscosity-effect. Thus for pure effusion the time for hydrogen should be very nearly one-quarter of that for oxygen, *i.e.* 3<sup>m</sup> 5<sup>s</sup>.3. It was found, however, that the effect of viscosity could be allowed for by employing, instead of the equation  $t = \kappa \sqrt{d}$ , where  $d$ =relative density and  $\kappa$ =a constant depending on the apparatus, the equation

$$t = \kappa_1 \sqrt{d} + \kappa_2 \mu,$$

where  $\mu$ =relative viscosity, and  $\kappa_1$ ,  $\kappa_2$ =apparatus-constants.

Thus if we employ the table of relative viscosities given by Graham \*, viz. :—

Oxygen . . . . .	= 1
Hydrogen . . . . .	= ·4375
Nitrogen or CO . . . . .	= ·8750
CO <sub>2</sub> . . . . .	= ·7272

we can use the results obtained with oxygen and hydrogen to calculate  $\kappa_1$  and  $\kappa_2$ . We obtain the equations

$$\begin{aligned} \kappa_1 \sqrt{1\cdot008} + \cdot4375 \kappa_2 &= 227\cdot9, \\ 4\kappa_1 + \kappa_2 &= 741\cdot3, \end{aligned}$$

from which

$$\kappa_1 = 129\cdot2, \quad \kappa_2 = 224\cdot4.$$

Hence the time of effusion for carbon monoxide should be given by

$$t = \sqrt{14} \cdot 129\cdot2 + \cdot875 \times 224\cdot2,$$

whence

$$t = 11^m 19^s.6.$$

The difference between this and the observed time is about 3 per cent. In the case of nitrogen the agreement is a

\* "On the Motion of Gases," Part II., Phil. Trans. 1849, pp. 349-392.

little closer, for here the calculated time is also  $11^m\ 19^{s.6}$ , while the mean observed time is  $11^m\ 17^{s.9}$ . A similar result is obtained by using von Obermaier's \* values for the relative viscosities. For the purpose of comparing argon and helium with oxygen it was necessary to reduce the viscosity-correction as much as possible, so no further experiments were carried out with this form of effusion-plug. Microscopic examination showed that the hole produced by the spark was irregular in shape and more of the nature of a series of cracks or fissures than anything else. These are no doubt of excessively minute width and so, even with thin-walled glass bulbs, relatively high viscosity-effects are unavoidable.

The new effusion-plug was made by taking a circular disk of platinum-foil (about  $\frac{1}{25}$  millim. thick), backing it with a flat piece of agate, and piercing it in the centre by gently pressing a very fine needle against it. The disks so constructed were then tested by sealing them to the end of a glass tube with Chatterton cement, and observing the rate of effusion into the exhausted vessel of a Töpler pump, by noting the rate of fall of the mercury in the vertical capillary.

A suitable disk having been obtained, it was melted off, burnt clean, and soldered with gold to the end of a stout platinum tube, which was finally sealed on to the end of the glass tube *w* (see figure). The effusion-aperture employed in the first series of measurements was about  $\frac{1}{50}$  millim. in diameter. Preliminary experiments showed that the time of effusion for any given gas varied somewhat from day to day and—to a less degree—even during the course of a consecutive series of measurements. This source of error was eliminated by comparing each gas directly with oxygen, and usually the time of effusion for oxygen was measured immediately before and immediately after that of the gas in question, and the mean of these two values taken.

The first effusion measurements were made with oxygen and hydrogen to enable the viscosity-correction to be applied. The results were as follows :—

$$\begin{array}{lll} \text{Oxygen} & 10^m\ 54^{s.7} & 10^m\ 54^{s.8},\ 10^m\ 54^{s.8}. \\ \text{Hydrogen} & 2^m\ 45^s. \end{array}$$

The time for hydrogen calculated from the densities alone is  $2^m\ 44^{s.4}$ . The apparatus is therefore practically free from viscosity and no correction is required.

The apparatus was left filled with hydrogen overnight, whereupon measurements of the effusion rate of hydrogen

\* *Wiener Berichte*, Bd. lxxiii.; *Carl's Repertorium*, Bd. xiii.

on the following day showed that some disturbance had occurred :—

	m.	s.
2	50·8	
2	51·5	
2	52·7	

It appears very probable that the platinum had occluded some hydrogen, and that the resulting volume-changes were the source of the variations. The apparatus was now allowed to remain exhausted overnight. Experiments with oxygen next morning gave the following results :—

	m.	s.
Half-an-hour after introduction of gas . . .	10	57·8
1½ hours " " " . . .	10	57·3
Apparatus left exhausted for an hour and fresh oxygen introduced . . . . .	10	56·5

The apparatus was left filled with oxygen overnight, pumped out the next morning, allowed to remain in connexion with the pump for an hour or so, and then refilled with oxygen :—

Oxygen . . . . . 10<sup>m</sup> 56<sup>s</sup>.2, 10<sup>m</sup> 56<sup>s</sup>.6.

It was accordingly concluded that the aperture had been again brought to a constant state and any occluded hydrogen removed. Argon was now measured :—

Oxygen . . . . . 10<sup>m</sup> 56<sup>s</sup>.4.

Argon . . . . . 11<sup>m</sup> 47<sup>s</sup>, 11<sup>m</sup> 47<sup>s</sup>.

According to the densities alone the time for argon should be

$$656\cdot4 \times \sqrt{\frac{19\cdot957}{16\cdot0}} = 12^m 13^s.1.$$

That is to say, argon effuses *too rapidly* by about 3·5 per cent. when compared with oxygen by the inverse square-root law.

In order to confirm this result a second determination was made. During the interval (week-end) the apparatus had remained exhausted and, as will be seen, the time of effusion for oxygen had considerably increased :

	m.	s.
Oxygen . . . . .	11	13·3
Argon . . . . .	12	3·9
Oxygen . . . . .	11	12
Mean oxygen . . . . .	11	12·6

The time for argon, calculated from that for oxygen by means of the densities, is 12<sup>m</sup> 31<sup>s</sup>.2, so that the observed time is 3·7 per cent. less, which agrees fairly well with the previous result.

This deviation being in the direction indicated by the adiabatic theory, the next thing was to measure some other gas with a diatomic molecule and specific-heat ratio 1·4; for in that case agreement might be expected between the observed and calculated values. Experiments with CO gave the following results:—

	m.	s.	m.	s.
Oxygen . . . . .	11	17·2		
CO . . . . .	10	29·5	10	30·6
Oxygen . . . . .	11	16		
Mean time for oxygen . . . . =		11	16·6	
Mean time for CO . . . . =		10	30	

The calculated value for CO is 10<sup>m</sup> 32<sup>s</sup>.9. The observed value is only ·4 per cent. smaller. Probably this deviation is due to experimental error (compare the two results with argon).

The next gas investigated was carbon dioxide; for as this possesses a lower specific-heat ratio than 1·4, its time of effusion ought to be *greater* than that calculated. Experiment proved the contrary:—

	m.	s.	m.	s.
Oxygen . . . . .	11	16·3		
CO <sub>2</sub> . . . . .	12	59	12	58·9
Oxygen . . . . .	11	15·3		
Mean value for oxygen . . . . .	11	15·8		

The value calculated for CO<sub>2</sub> is

$$675\cdot8 \times \frac{\sqrt{22}}{4} = 13^m 12^s.$$

The observed time is 1·7 per cent. *less*.

This was confirmed by a second measurement with a fresh preparation of CO<sub>2</sub>:—

	m.	s.
Oxygen . . . . .	11	18·7
CO <sub>2</sub> . . . . .	13	2
Oxygen . . . . .	11	18
Calculated for CO <sub>2</sub> from oxygen	13	15·4

Here, again, the observed time per cent. is 1·7 per cent. less.

This deviation \* being in the opposite direction to that indicated by the adiabatic theory, it was considered advisable

\* Graham found a similar deviation in the case of CO<sub>2</sub>. He used brine, however, instead of mercury as enclosing fluid, and ascribed the deviation to the solution of the CO<sub>2</sub> in the brine (a single experiment lasted about an hour).

to re-examine the viscosity-relations of the apparatus. Results :—

	m.	s.
Oxygen . . . . .	11	16
Hydrogen . . . . .	2	51·6
Oxygen . . . . .	11	16
Calculated for hydrogen by densities . . . . .	2	49·7

These results indicate the presence of a small viscosity-effect. This was probably caused by the gradual narrowing of the aperture, which is shown by the successive results for oxygen. Now all the previous calculations have assumed the absence of any disturbance due to viscosity. The best way to determine their value is to re-calculate the experimental results, introducing a correction for viscosity as determined by these last measurements, *i.e.* introducing a *maximum* correction. This could be done directly by means of the formula

$$t = \kappa_1 \sqrt{d} + \kappa_2 \mu,$$

provided  $\kappa_1$  and  $\kappa_2$  remained constant. But the results for oxygen show that this was not the case. It is probable, however, that any change in the size of the hole will chiefly affect  $\kappa_1$ , since the outflow is mainly an "effusion" flow. These considerations suggest the following method of making the viscosity-correction. Calculate values for  $\kappa_1$  and  $\kappa_2$  from the last measurements for oxygen and hydrogen. Then in any particular case correct the value of  $\kappa_1$  so obtained by assuming that the change in  $\kappa_1$  is proportional to the change in the observed time of effusion for oxygen. That this mode of procedure is justifiable is shown by the fact that the times calculated for oxygen with the values of  $\kappa_1$  and  $\kappa_2$  so obtained agree very closely with the observed times in each particular case.

The last results for oxygen and hydrogen give  $\kappa_1 = 166\cdot5$ ,  $\kappa_2 = 10$ . Accordingly the corrected time for CO (see p. 435) is given by

$$t = \left( 166\cdot5 \times \frac{676\cdot6}{676\cdot0} \times \sqrt{14} \right) + (875 \times 10),$$

whence

$$t = 10^{\text{m}} 32\text{s}.3.$$

The following short table will serve to show the extent to which the correction affects the results :—

	m. s.	m. s.	m. s.	per cent.
Argon* .....	12 3·9	12 31·2	12 31	3·6
Carbon monoxide ...	10 30	10 32·9	10 32·3	0·36
Carbon dioxide... ....	13 2	13 15·4	13 11	1·1

The first column gives the observed time, the second the time calculated from the densities alone, the third the calculated time corrected for viscosity, and the fourth the percentage deviation of the observed time from the time so corrected. In the case of argon and carbon monoxide the correction is quite negligible. For CO<sub>2</sub> it amounts only to 5 per cent. The conclusions previously drawn remain therefore unaffected.

With regard to CO<sub>2</sub>, the want of agreement between theory and experiment may possibly be due to the fact that this gas departs too much from the simple laws of the ideal gas.

In the case of argon the time of effusion, as calculated from that of oxygen according to the theory given by Hugoniot and Osborne Reynolds, is 11<sup>m</sup> 55<sup>s</sup>†. It is only to be expected that the observed value would be greater, as the phenomenon is probably something intermediate between isothermal and adiabatic‡.

\* The viscosity of argon referred to oxygen was obtained by combining Lord Rayleigh's value referred to air with Graham's value of air referred to oxygen. The result is 1·21 × 901 = 1·09.

† According to Parenty's formula, it is 11<sup>m</sup> 31<sup>s</sup> 7.

‡ A few words of explanation are necessary here. In the first place, the mass-efflux on the assumption that the phenomenon is *isothermal* may be found as follows:—Employing the equation  $\int \frac{dp}{\rho} + \frac{1}{2}q^2 = \text{const.}$ , which holds along a stream-line for steady irrotational motion, we obtain on integrating, since  $p = \rho RT$ ,  $q = \sqrt{2RT \log \frac{\rho_0}{\rho}}$ , where  $\rho_0$  = density of quiescent gas in the reservoir. If the velocity, density, and sectional area at the vena contracta be denoted by  $q'$ ,  $\rho'$ , and  $S'$  respectively, then mass-efflux  $= q' \rho' S'$ . From the condition  $\frac{d}{dp}(q\rho) = 0$ , we find  $\log \frac{\rho_0}{\rho} = \frac{1}{2}$  and therefore  $S' q' \rho' = \frac{S' \rho_0}{\sqrt{eRT}}$ . Thus comparing two gases between the same pressure-limits during the period of constant efflux,  $\frac{t_1}{t_2} = \sqrt{\frac{\rho_1}{\rho_2}}$ , as already stated.

The equation given by Parenty being based neither on the assumption of an adiabatic nor an isothermal efflux, and being in fact practically an empirical equation, not much importance need be attached to the fact that it yields a value which is very sensibly smaller than that observed.

It must be noted that on the assumption of constant temperature, the velocity of the gas at the vena contracta is *less* than the velocity of sound in gas of that density and pressure, being in fact equal to the Newtonian value.

A sample of helium was now introduced into the apparatus. After the effusion had proceeded for a short time, a complete block occurred. The helium was pumped out, and the mercury having been sucked out of the seal, the apparatus was cut above the tap and the effusion-plug removed for examination. There was a whitish deposit on the platinum. The hole was cleared by cautiously heating the platinum to redness and drawing air through it. On sealing the apparatus together again the hole was found to be clear, but on again admitting the helium another block occurred. It was evident that the helium contained some impurity which attacked the platinum or condensed in some way in the aperture. The helium was accordingly removed and the hole again cleared out as described. On sealing together again and testing with oxygen and hydrogen, a greatly increased viscosity-effect was observable. When the effusion-tube was cut out and the platinum foil microscopically examined, the cause of the viscosity could be seen in the form of *two* holes connected by a fissure. This was probably due to the corroding action of the impurity \* combined with the frequent heating.

A new disk of foil was now pierced and soldered on to the platinum tube; but it was also found to show a very high viscosity-effect. The origin of this was finally traced to the cracking of the enamel at the junction of the platinum and glass tubes.

Owing to the difficulty of making this joint, a new effusion-plug was constructed as follows:—A thick circular disk of platinum was made by welding several pieces of foil together. A circular hole was punched in the centre of this, and a thin † disk of foil, which had been punctured in the manner previously described, was welded on so as to cover the hole in the thick disk. The latter was then fastened by means of Chatterton cement to a glass tube whose end had been turned over and ground to a flat flange; and this tube was sealed to the rest of the apparatus. After some trials an effusion-plug was obtained which showed only a comparatively small viscosity-effect:—

		m.	s.	m.	s.
Oxygen . . . .	4	3·1			
Hydrogen . . . .	1	2·2	1	3·3	
Oxygen . . . .	4	3			

\* A piece of glass which was immersed in the helium was found to fume in the air. As oxygen had been previously removed from the helium by burning phosphorus, the impurity was probably some volatile lower oxide of phosphorus.

† This was the thinnest foil procurable from Johnson and Matthey that was free from microscopic holes. It was about  $\frac{1}{1000}$  in. thick.

A repetition of this test on the following day gave :—

	m.	s.
Oxygen . . . . .	4	2·9
Hydrogen . . . . .	1	3·3

These results lead to a much higher viscosity-correction than in the case of the effusion-plug first used. We get  $\kappa_1 = 57\cdot6$ ,  $\kappa_2 = 12\cdot4$ . Measurements with cyanogen gave the following results :—

	m.	s.	m.	s.
Oxygen . . . . .	4	5		
Cyanogen . . . . .	5	4·9	5	4·2
Oxygen . . . . .	4	4		
Mean time for Cyanogen .	5	4·6		

Graham gives  $506$  for the viscosity of cyanogen referred to oxygen. The calculated value is therefore

$$t = \left( \sqrt{26} \times 57\cdot6 \times \frac{244\cdot5}{243\cdot0} \right) + (12\cdot4 \times 506) = 5^m 1^s 8.$$

There is a deviation here of  $9$  per cent. in the direction of *slower* effusion. The time calculated from the densities alone is  $5^m 11^s 6$ .

The helium previously used was sparked over potash with oxygen and the oxygen removed by heated copper. After being dried by  $P_2O_5$  it gave the following results :—

	m.	s.
Oxygen . . . . .	4	3·8
Helium . . . . .	1	37·1
Oxygen . . . . .	4	3·4

The viscosity of helium referred to air was found by Lord Rayleigh to be  $96$ , so that its value referred to oxygen is  $865$ . The density of this specimen of helium was determined and found to be  $2\cdot314$ , so that it contained a considerable amount of argon. The calculated time is  $1^m 38\cdot6$ , from which it would appear that the helium effuses  $1\cdot5$  per cent. faster than as calculated. This helium after being further dried over  $P_2O_5$  was examined again, with the following result :—

	m.	s.
Oxygen . . . . .	4	3·2
Helium . . . . .	1	37·6
Oxygen . . . . .	4	4·0
Helium (calc.) . . . . .	1	38·4
Helium (calc. from density only) . .	1	32·6

Here the deviation only amounts to  $8$  per cent., which is about half the previous amount. Possibly this want of agreement in the results is partly due to the increased likelihood of

error in noting the points of passage owing to the very rapid rate of effusion.

Owing to the high viscosity-correction it was thought advisable to re-measure argon and carbon monoxide as a check on the results given by this effusion-plug. Results:—

	m.	s.
Oxygen . . . .	4	3·8
Argon . . . .	4	21·1 (density 19·71)
Oxygen . . . .	4	3·4
Argon (calc.) . . .	4	29·9 3·3 per cent. faster.
Oxygen . . . .	4	3·2
CO . . . .	3	46·4
Oxygen . . . .	4	3·4
CO (calc.) . . .	3	46·6

These results are in fairly close accordance with those previously obtained\*, so that the method of correcting for viscosity appears to be justified in the main.

Owing, however, to the unpleasant prominence of the viscosity-correction in the case of helium, several attempts were made to obtain a better effusion-plug. An aperture was finally obtained showing a much smaller viscosity-effect. The pierced disk of thin foil was sealed transversely in a tube of flint-glass and the latter sealed on to the rest of the apparatus. This forms the simplest and most secure method of attaching the platinum-foil disk to the effusion apparatus. With hydrogen and oxygen the following results were obtained:—

	m.	s.
Hydrogen . . .	2	7·9
Oxygen . . .	8	21·3

The time for hydrogen calculated from the densities is  $2^m\ 5^s\cdot8$ , so that a small viscosity-effect still exists. These results give  $\kappa_1=122\cdot5$ ,  $\kappa_2=11\cdot3$ . Helium and argon were now remeasured.

#### Helium.—Density 2·314.

	m.	s.	m.	s.
Oxygen . . . .	8	22·2		
Helium . . . .	3	16·8,	3	16·6
Oxygen . . . .	8	24·2		

	m.	s.
Mean time for He observed . . . .	3	16·7
Time calculated with viscosity-correction	3	16·7
"      "      from densities alone . .	3	11·2

\* As evidenced by the density, this specimen of argon was not very pure. It probably contained some hydrogen. This would account for the rather low "deviation" of 3·3 per cent.

*Argon*.—Density 19.71.

	m.	s.	m.	s.
Oxygen . . . . .	8	24.2		
Argon . . . . .	9	0.6,	8	59.5
Oxygen . . . . .	8	23.8		
Mean time for argon (observed) . . . . .	9	0		
Calculated from densities alone . . . . .	9	19.4		
,, with viscosity-correction . . . . .	9	19.2		

These results show that in the case of argon the correction is negligible and that the observed time is 3.4 per cent. less than the calculated time, which is in good agreement with former results. In the case of helium the viscosity correction is still considerable and, contrary to previous results, the observed and calculated values agree.

After these measurements the times for oxygen and hydrogen were again determined:—

	m.	s.	m.	s.
Oxygen . . . . .	8	23.9		
Hydrogen. . . . .	2	6.6,	2	6.8
Oxygen . . . . .	8	23.3		

The time for hydrogen calculated from the densities is 2<sup>m</sup> 6<sup>s</sup> 4, so that there now appeared to be practically *no* viscosity-effect. Under these circumstances it appears difficult to say what sort of correction ought to be applied to the last-obtained results for helium. In order to try and clear up this difficulty a fresh series of measurements was made, with the following results:—

*Argon*.—Pure specimen, density 19.96.

	m.	s.
Argon . . . . . . . . . . .	9	1.4
Mean oxygen . . . . . . . . .	8	22.8
Argon (from densities) . . . . .	9	21.6
Argon (corrected for viscosity) .	9	21.4

Observed rate 3.5 per cent. faster than calculated rate.

*Helium*.—Purer specimen, density 2.139.

	m.	s.
Oxygen . . . . .	8	22.8
Helium . . . . .	3	7.8
Oxygen . . . . .	8	22.6
Helium (calculated from densities) . . .	3	3.8
Helium (with viscosity correction) . . .	3	9.4

*Carbon monoxide.*

	m.	s.	m.	s.
Oxygen . . .	8	23·6		
CO . . .	7	49·8,	7	49·2
Oxygen . . .	8	22·7		
Mean time for CO . . . . .			7	49·5
Time calculated from densities . .			7	50·7
Time calculated with viscosity . .			7	49·9

The results obtained for argon and carbon monoxide are in agreement with former ones. If we apply no viscosity-correction, then the helium effuses *slower* than as calculated. The want of agreement between this and former results may be partly due to variable admixture with argon.

The fact remains that all the results obtained for helium are affected by a more or less uncertain correction for viscosity, and do not agree among themselves. If any one were to be selected as better than the rest, it would be the last one, as the hole appeared to be practically free from viscosity-effects in this case, and the specimen of helium was pretty pure.

*Saint-Venant and Wantzel's Phenomenon.*

It was stated at the beginning that the dimensions of the apparatus were chosen so that the measurements lay in the region where the rate of effusion was independent of the back-pressure. This was frequently confirmed by experiment. The following results, obtained in the last series (where the back-pressure rose from 0 to 47·5 millim. during the course of a measurement), will serve to confirm the statement made above.

*Oxygen.*

Time of Effusion.	Back-pressure.
m. 8 23·3	0 -47·5
8 23·5	47·5-93·9
8 25·3	93·9- —

In this series of experiments the final back-pressure was 47·5 millim. as already stated, and the initial and final pressures in the gas-reservoir 525 millim. and 322 millim. respectively. In the other series the final back-pressure was

60 millim., and the initial and final pressures in the gas-reservoir 690 millim. and 484 millim. These numbers are only approximate and intended merely to show the pressure-conditions under which the experiments were conducted.

### The Joule-Thomson Effect.

As foreseen by the theory, the rate of effusion of argon, when compared with that of oxygen, is very considerably greater than the value as calculated by the law of the inverse square root of the density. The foregoing experiments agree uniformly in showing that the deviation amounts to  $3\frac{1}{2}$  per cent. On the other hand, the results obtained with helium, although not very uniform, show pretty conclusively that its behaviour is unlike that of argon. According to the theory, however, it should behave in an exactly similar manner. These facts seem to point to the omission of some factor or factors in the basis of the theory.

Now it will be observed that the theory assumes that the gases obey the ideal gas laws, and hence excludes anything of the nature of the Joule-Thomson effect. It therefore appeared of interest to examine the question of the effusion of an *imperfect* gas, with special reference to the Joule-Thomson effect.

An application of the equation of continuity and the law of conservation of energy to the issuing jet yields the well-known fundamental equation :—

$$\frac{1}{2}q^2 + U + pv = \text{const.},$$

where  $q$  = velocity,

$U$  = internal energy per unit of mass,

$v$  = specific volume,

$p$  = pressure.

It is possible\* to find an approximate expression for  $U$  by making use of the equation given by Joule and Thomson†, namely:—

$$dT = \frac{K}{T^2} dp. \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

Choosing  $p$  and  $T$  as independent variables, we have

$$\frac{\partial}{\partial p} (U + pv) dp + \frac{\partial}{\partial T} (U + pv) dT = 0. \quad \dots \quad \dots \quad (2)$$

\* Cf. Poincaré, *Thermodynamique*.

† For the present purpose it was not thought necessary to use the formulæ recently proposed by Rose-Innes (Phil. Mag. March 1898), and by Love (Proc. Phys. Soc. vol. xvi. Dec. 1899, p. 454).

If we were dealing with an ideal gas, we should have

$$U + pv = CT, \text{ and } \frac{\partial}{\partial t} (U + pv) = C,$$

where  $C$  = specific heat at constant pressure. This is not strictly applicable to the present case, but we may introduce it into (1) and obtain an approximation. From (1) and (2) we therefore obtain

$$\frac{\partial}{\partial p} (U + pv) = -\frac{KC}{T^2},$$

which on integration gives

$$U + pv = -\frac{KCp}{T^2} + f(T). . . . . \quad (3)$$

Employing (3) and the fundamental equation given above, we obtain an expression for the velocity of effusion which involves the constant of the Joule-Thomson equation :—

$$q^2 = 2[f(T_0) - f(T)] + 2KC\left(\frac{p}{T^2} - \frac{p_0}{T_0^2}\right). . . . \quad (4)$$

For an ideal gas  $K=0$  and  $f(T)=CT$ . We may therefore write approximately :—

$$q^2 = 2C(T_0 - T) + 2KC\left(\frac{p}{T^2} - \frac{p_0}{T_0^2}\right).$$

The first term on the right-hand side was given by Saint-Venant and Wantzel. The second term appears, therefore, as a *correction-term* in a form involving the Joule-Thomson constant. The equation may also be written in the form

$$q^2 = \frac{2\gamma}{\gamma-1} \left( \frac{p_0}{\rho_0} - \frac{p}{\rho} \right) + 2KC\left(\frac{p}{T^2} - \frac{p_0}{T_0^2}\right).$$

It is important to determine the *sign* of the correction-term. To do this it appears justifiable to assume the ideal gas laws, and so one has

$$\begin{aligned} 2KC\left(\frac{p}{T^2} - \frac{p_0}{T_0^2}\right) &= 2KCR\left(\frac{\rho}{T} - \frac{\rho_0}{T_0}\right) \\ &= 2KCR\frac{\rho_0}{T_0} \left[ \left(\frac{\rho}{\rho_0}\right)^{2-\gamma} - 1 \right]. \end{aligned}$$

Consider first the region where  $2 > \frac{\rho_0}{\rho} > 1$ . Since  $\frac{\rho}{\rho_0} = \left(\frac{\rho_0}{p}\right)^{\frac{1}{\gamma}}$ , it is clear that the expression in square brackets

is *positive*. Consider next the region where the efflux is independent of the back-pressure.

From the equation

$$q^2 = \frac{2\gamma}{\gamma-1} \left( \frac{p_0}{\rho_0} - \frac{p}{\rho} \right) + 2\text{KCR} \frac{\rho_0}{T_0} \left( \frac{\rho^{2-\gamma}}{\rho_0^{2-\gamma}} - 1 \right)$$

we obtain

$$q^2 \rho^2 = \frac{2\gamma}{\gamma-1} \left( \rho^2 \frac{p_0}{\rho_0} - k \rho^{\gamma+1} \right) + 2\text{KCR} \frac{\rho_0}{T_0} \left( \frac{\rho^{4-\gamma}}{\rho_0^{2-\gamma}} - \rho^2 \right),$$

where the laws of the ideal gas are assumed, and  $\frac{p}{\rho^\gamma} = k$ . To obtain the value of  $\rho$  at the vena contracta, it is necessary to differentiate with respect to  $\rho$  and equate to zero. This leads to the equation in  $\rho$ :—

$$\frac{\gamma}{\gamma-1} \left[ 2 \frac{p_0}{\rho_0} - (\gamma+1) k \rho^{\gamma-1} \right] + \text{KCR} \frac{\rho_0}{T_0} \left[ \frac{(4-\gamma)\rho^{2-\gamma}}{\rho_0^{2-\gamma}} - 2 \right] = 0.$$

This equation is unfortunately not directly solvable; but its actual solution is unnecessary for the present purpose. The value of  $\rho$  given by it when substituted in the right-hand member of the preceding equation gives  $q\rho$  at the vena contracta, and this multiplied by the sectional area  $S'$  of the jet at that point gives the mass-efflux. From the above it is clear that in this case too the sign of the correction-term depends on K and the expression  $\left[ \left( \frac{\rho'}{\rho_0} \right)^{2-\gamma} - 1 \right]$ . As before,

we find that this expression is positive, since  $\frac{p_0}{p'} > 1$ , where  $p'$ ,  $\rho'$  denote the pressure and density at the vena contracta. The final result may be stated as follows:—"A gas will effuse *more rapidly* or *more slowly* than an ideal gas of equal density according as K is *positive* or *negative*."

Now Joule and Thomson found K to be *positive* for all gases, with the exception perhaps of hydrogen. For hydrogen K was very small and its sign rather uncertain. Accordingly most gases will effuse in some degree *faster* than the usual theory of efflux would indicate. Now helium \* is even more "perfect" than hydrogen. It is therefore just possible that for helium K is *negative*, in which case helium would effuse somewhat more *slowly* than the ordinary theory would indicate.

How far these effects would compensate each other, and in particular what the relative importance of the correction-term is, I have not yet investigated, but hope to do so in a subsequent communication.

\* This has been shown by Professor Ramsay and Dr. Travers in a set of experiments (not yet published) on the compressibility of helium.

*Summary of Results.*

1. Argon is found to effuse, when compared with oxygen,  $3\frac{1}{2}$  per cent. *faster* than as calculated by the law of the inverse square root of the density. This result is independent of any masking effect due to viscosity.

2. This result is in *qualitative* agreement with the adiabatic theory of the efflux of ideal gases, and is, if this may be granted, a confirmation of the high specific-heat ratio of argon.

3. When viscosity-effects are eliminated or allowed for, it is found that hydrogen, oxygen, and carbon monoxide effuse relatively in the manner predicted by the theory for ideal gases possessing the same, or nearly the same, specific-heat ratio.

4. Carbon dioxide, when compared with oxygen, appears to effuse about 1 per cent. *faster* than as calculated from the densities. This result is not in accordance with the adiabatic theory of the efflux of *ideal* gases.

5. The results obtained for helium are not uniform, and are affected by a viscosity-correction depending on an empirical formula. They are sufficient, however, to show that the behaviour of helium is unlike that of argon, a result which is not foreseen by the theory.

6. If account be taken of the deviation of ordinary gases from the ideal laws, it is possible to obtain an expression for the efflux which contains a correction-term involving the constant K of the Joule-Thomson effect.

7. The sign of this correction-term shows that a real gas will effuse more *rapidly* or more *slowly* than an ideal gas of equal density and specific-heat ratio, according as K is *positive* or *negative*.

8. The suggestion is made that possibly the anomalous results obtained with carbon dioxide and helium may be thus explained. The deviations of the observed results from the results calculated for an ideal gas are, in the case of CO<sub>2</sub>, in *qualitative* accordance with the theory proposed. In the case of helium they would be so if that gas possessed a negative K.

In conclusion I desire to express my deep sense of obligation to Professor Ramsay, at whose suggestion this investigation was begun, and whose valuable advice and assistance I enjoyed throughout its course.

I wish also to thank Dr. Travers for kind advice on many occasions. To Mr. E. C. C. Baly's great skill and constant advice and assistance I am more indebted than I can possibly say.

Chemical Laboratory,  
University College, London.  
December 1899.

**XLII.** *On some Improved Formulae and Methods connected with Lenses.* By THOMAS H. BLAKESLEY\*.

IN a paper read before the Physical Society on June 11th, 1897, I pointed out the connexion between the distance of an object from the first principal focus of a lens and the relation of its linear magnitude with that of the image produced : viz. that every change in that distance by the amount of the focal length of the lens produced a unit of change in the relation of these magnitudes ; and I described methods by means of which the focal length might be very accurately determined upon these grounds.

I also explained how the position of the two principal foci might be accurately determined by placing the lens upon a plane mirror and finding the spot at which if an object be placed its image inverted will coincide with it.

The rules given apply equally well to combinations of coaxial lenses as to single lenses.

Hence all focussing properties of lens-systems are really determined when the three following matters are known :—

- (1) The focal length with proper sign.
- (2) The position of the first principal focus.
- (3) The position of the second principal focus.

The *first* principal focus is defined as the point such that if a beam of light *before* impact on the lens-system is diverging from it or converging to it, then *after* passage through the system the beam will consist of parallel rays.

The *second* principal focus is the point such that if *before* impact the beam is one of parallel rays, *after* passage it will consist of rays either diverging from or converging to that point.

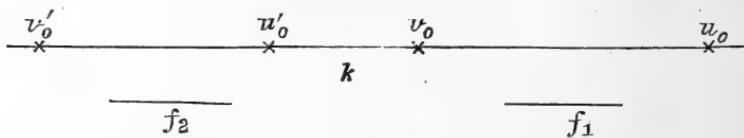
In the present communication I wish to point out the rules by means of which, when these elements are known for any two systems, the elements for the combination of the two systems are readily obtained.

Each lens of course carries its own system of points with it, but an independent variable is necessarily introduced in combining systems at different distances.

The simplest magnitude will be found to be the distance between the second principal focus of the first system and the first principal focus of the second system, which I call  $k$ , and which has a positive value in the direction of the propagation of light.

\* Communicated by the Physical Society : read December 8, 1899.

Let  $u_0, v_0$  be the positions of the principal foci of the first system, and  $u'_0, v'_0$  those of the second system, light being supposed to come from the right.



Let  $f_1, f_2$  be the two focal lengths, and the length from  $v_0$  to  $u'_0$  be  $k$ .

Then the following rules fix the elements of the whole united system.

The new first principal focus is distant from  $u_0$  towards the right hand  $\frac{f_1^2}{k}$ .

The new second principal focus is distant from  $v_0$  towards the left hand  $\frac{f_2^2}{k}$ .

The new focal length is  $\frac{f_1 f_2}{k}$ .

These rules are virtually equivalent to the following statements:—

The new first principal focus is conjugate by the first system with the first principal focus of the second system.

The new second principal focus is conjugate by the second system with the second principal focus of the first system.

The points  $u_0, v'_0$  are conjugate with one another. The travel of the principal focus from  $u_0$  to its final position being easily and accurately determinable by experiment, and having for its theoretical value  $\frac{f_1^2}{k}$ , it may be employed in a variety of practical ways.

The following example may illustrate how it may be used to find the focal length of a lens in the absence of a magnification apparatus.

The tubes of a telescope retaining the object-glass, but otherwise free from lenses, are placed vertically with the object-glass downwards upon a plane mirror. Crossed silk fibres are stretched across the open end, and the tubes are adjusted till the image of these fibres is in the same horizontal plane as the fibres themselves. The length of the tubes is then found to be 25.95 cms. An achromatic telescope object-glass, whose principal foci are known to be 21.12 and 19.92 from the convex and plane sides respectively, is placed upon the upper end of the telescope-tube before mentioned, the plane side being downwards. A minute triangle of white paper

(about 3 sq. mm. in area) is placed in the centre of the upper or convex side, and the tubes of the telescope, still standing on the plane mirror, are manœuvred until the image of this paper coincides with itself. The length is then found to be 25·15 cm. The focal length of this lens can then be determined as follows:—

The principal focus of the lower lens is above the lower surface of the upper lens by the amount of the shortening of the tubes, *i. e.* 25·95 – 25·15, or ·80. But the position of the second principal focus of the upper lens is 19·92 below this face. Therefore the value of  $k$  is  $-(19\cdot92 + \cdot80) = -20\cdot72$ , the negative value being the result of overlap in regard to the two systems.

But the amount by which the outer principal focus moves upwards is – 21·12.

Hence

$$\frac{f_1^2}{-20\cdot72} = -21\cdot12.$$

Hence  $f_1 = -20\cdot92$ , the negative sign being of course chosen.

Again, if a convex lens, whether achromatic or not, is laid upon a plane mirror, its convex side downwards, a few drops of any refracting liquid being placed between the two, the principal focus will travel a distance depending on the index of refraction of the liquid. Care must be taken that the combination is convex in character.

If  $r$  is the radius of the face common to the lens and the liquid and  $\mu$  is the index of refraction of the liquid, the liquid lens will have for focal length  $\frac{r}{\mu-1}$ , and its first principal focus will be situated at  $\frac{r}{\mu-1}$  below the plane mirror. If  $v_0$  be taken as the distance from the wetted surface of the lens of its own second principal focus, the  $k$  of this problem is clearly  $\left\{ \frac{r}{\mu-1} - v_0 \right\}$ .

Hence if  $f$  be the focal length of the lens, and  $c$  be the travel of the first principal focus due to the insertion of the liquid,

$$\frac{f^2}{\frac{r}{\mu-1} - v_0} = c,$$

or

$$\frac{1}{r} \left( \frac{f^2}{c} + v_0 \right) = \frac{1}{\mu-1}.$$

If the lens constants are thoroughly known, we have an equation of the form

$$\frac{1}{\mu-1} = \frac{A}{c} + B,$$

where A and B are both constants.

In practice it would be possible to determine A and B by observing the values of  $c$  in the cases of two liquids whose indices have been determined in other ways; but it is not necessary to take this course where a single lens is employed, because in that case the radius  $r$  can be expressed in terms of the focal length, the distances  $u_0$  and  $v_0$  of the principal foci from the anterior and posterior surfaces of the lens, and the thickness of the lens, the latter being easily measured by calipers. The formula for  $\frac{1}{r}$  then is

$$\frac{u_0 + f}{f^2 - u_0 v_0 + df},$$

which can be inserted in the above equation.

Or if a compound lens is employed, the value of  $r$  may be determined by a spherometer; but this instrument does not furnish the most accurate means of calculating such radii. This point will receive attention below.

A telescope is an arrangement of coaxial lenses, some forming what is called the object-glass, others the eyepiece. Each of these portions may be far from simple, but each must have its own focal length and pair of principal foci. When the second principal focus of the object-glass coincides with the first principal focus of the eyepiece, the focal length of the combination is infinite, for the  $k$  of this problem is equal to zero. This is often considered to be the position of adjustment for viewing distant objects; and in fact a telescope will always have a very long focal length though the actual value will differ with different eyes. Now if a telescope is in this condition of adjustment, having an infinite focal length, we may divide the system anywhere we please, and call one part the object-glass and the other the eyepiece. All that is necessary is that the dividing surface shall be a plane at right angles to the common axis, or a sphere having its centre on the common axis. The division itself may even take place through one of the lenses.

The two portions of the system thus formed will have the following properties.

The second principal focus of one of them will always coincide with the first principal focus of the other.

The ratio of the two focal lengths will always have the same value, the magnifying-power of the whole, wherever the division is made.

When, for the purposes of celestial photography, a telescope has a camera attached at the eye-end, the question arises how far the eyepiece must be racked out in order to obtain an image on the plate.

If the optical properties of the eyepiece are known, *i. e.* its focal length and the positions of its principal foci, then of course the distance of the camera-plate from the second principal focus is known. But the camera-plate must be in the second principal focus of the whole system. Hence the distance from the second principal focus of the eyepiece to the plate must be the travel of the principal focus due to the application of the object-glass, *i. e.*

$$\frac{f^2}{c} = k,$$

where  $f$  is the focal length of the eyepiece,  $c$  is the distance of the photographic plate from the second principal focus of the eyepiece, and  $k$  is the amount of racking out required from the position in which the focal length of the telescope is infinite.

If we have a lens system, and coaxial with it a mirror, either plane or spherical, and light is passed first through the lens in a direction towards the mirror, and after reflexion at the mirror, back through the lens in the reverse direction, the combination forms a virtual mirror to which the following very simple rules apply:—

The virtual mirror's surface is conjugate with the real mirror's surface by the lens.

The virtual mirror's centre of curvature is conjugate with the real mirror's centre of curvature by the lens.

These rules enable one at once to determine the general facts of the image-formation in any given case.

If the virtual mirror is a plane one, its radius of curvature is infinite, and either its surface or its centre of curvature must be at infinity, while the other must be at a finite distance.

Hence to form a virtual plane mirror either the surface or the centre of the real mirror must be in the second principal focus of the lens.

If the surface of the mirror makes this coincidence, the surface of the plane virtual mirror will be at infinity; but its centre is not so, and may be easily found experimentally, as

the place where an object coincides with an *inverted* image of itself.

If the centre of curvature of the mirror coincides with the second principal focus of the lens, the centre of the curvature of the virtual plane mirror is at infinity; but the plane itself will not be so, and its position may be easily found experimentally as the place where an object coincides with an *erect* image of itself.

Such virtual mirrors, whether plane or not, giving erect images, are of course often formed in front of the lens; and in such cases there is not the smallest difficulty in passing an object "through the looking-glass."

The rules given above for the position of the centre of curvature and surface of the virtual mirror are equivalent to the two following mathematical formulæ:—

The surface of the virtual mirror is situated at a distance from the first principal focus of the lens equal to  $\frac{f^2}{k + \frac{r}{2}}$

in a direction contrary to that in which the light is going *before* reflexion; and the centre of curvature of the virtual mirror is situated at a distance from the same point equal to  $\frac{f^2}{k - \frac{r}{2}}$  measured positively in the same direction.

In these formulæ  $f$  is the focal length of the lens;  $r$  is the radius of curvature of the mirror (positive if concave);  $k$  is the distance from the second principal focus of the lens to the principal focus of the mirror, measured positively in the direction in which light is proceeding before reflexion.

Now suppose that the mirror coincides in curvature and position with the second face of the lens. This will be the case if either that face is silvered or placed in a pool of mercury.

The position of the centre of curvature of the virtual mirror can be found in the usual way, by coincidence with inversion of the image and object. Let it be distant  $c$  from the original first principal focus of the lens, positively measured in the direction opposite to the light before reflexion.

Then by the above formula

$$\therefore c = \frac{f^2}{k - \frac{r}{2}};$$

But if  $v_0$  be the distance of the second principal focus of the lens from the second surface, the value of  $k$  will be

$$-\left\{ v_0 + \frac{r}{2} \right\}.$$

Hence

$$c = -\frac{f^2}{v_0 + r} \text{ or } r = -\frac{f^2}{c} - v_0;$$

all the symbols on the right hand of this last equation are known.

This affords a very convenient way of practically measuring the radius of curvature of the face of a lens, as a pool of mercury is an easy way of producing the conditions.

I have mentioned above in dealing with the index of refraction of a liquid that a knowledge of this value is important; and this optical method is in my opinion far superior to that of the spherometer in making the determination.

Those who may have followed the above remarks with care will see that I strongly advocate those optical methods of measurement which depend upon making a coincidence between the position of an object and that of its image. These coincidences may be determined with very great precision by any one accustomed to observation; and the apparatus required, though it may be made as elaborate as any others, need be no more than the simplest. A small optical bank about five inches long, a holder to slide up and down and to carry a sharply-pointed piece of white paper, four square inches of good plane mirror, a hand-lens of about 2 inches focal length to determine coincidences, and a rule and calipers to measure distances, are really all that is necessary to make determinations of an accuracy far surpassing that in vogue at present.

I have examined a lantern-projector which professed to have a focal length of 6 inches ( $= 15.24$  cm.). It actually possesses one of 17.81 cm.

A microscope objective whose nominal value was  $1\frac{1}{2}$  inch, made by the most eminent optician in London, was measured directly, and indirectly by taking its two component lenses separately and measuring their focal lengths and the overlap of their principal foci.

The first method gave 1.347 } inches focal length.  
 „ second „ 1.355 }

The nominal value was therefore certainly in error by as much as 10 per cent.

**XLIII. On the Controversy concerning Volta's Contact Force.**  
*By Professor OLIVER LODGE, D.Sc., LL.D., F.R.S.*

[Continued from page 388.]

**CHAPTER IV. (continued).**

*Osmotic Pressure-or Diffusion Views of a Voltaic Cell.*

THE osmotic pressure hypothesis, strictly speaking, perhaps hardly belongs to my present subject, since whatever controversy or question has gathered round it is of a different kind from that concerning the seat of the E.M.F. The osmotic pressure hypothesis does not concern itself apparently with the Volta electrostatic effect, but with the mechanism of propulsion in a voltaic cell : it hardly cares to discriminate between the two cases, for they appear in many respects much the same; and it locates the seat of the E.M.F. quite definitely at a junction on one side of which at least there is a liquid or substance with loco-mobile atoms, and not at a metal-metal junction: it deals entirely with moving ions, such as cannot exist in true solids. Moreover it is not a hypothesis really distinct from that of the recognized chemical combination associated with a current-producing cell, only it regards that chemical combination from a different point of view—from the dissociation or ionisation point of view. Instead of saying that zinc is oxidised or that zinc sulphate is formed, it professes to regard atoms of zinc as shot off into the liquid in a non-combined or free form: ultimately, no doubt, to enter into real combination, but existing for a time, and always in a certain proportion, in the form of practically free ions. Thus the full discussion of the osmotic pressure hypothesis is essentially chemical in its nature, and need not here concern us. At the same time so many people are interested just now in this remarkable view of chemical combination, that I refrain from passing it by altogether ; though, as it is not a hypothesis specially and long familiar to me, my remarks on it will not have any particular weight. Fortunately there are several writings to which a student of such matters can be referred—the treatise of van t' Hoff, the work of Arrhenius and of Planck, and the textbooks of Ostwald and of Nernst, especially of Nernst ; and likewise the excellent Report on these subjects presented to the British Association in 1897 at Toronto by Mr. W. C. D. Whetham, as well as to his book on 'Solution.' Furthermore, I may refer to the works of Dr. J. Larmor, especially Phil. Trans. vol. cxc. p. 270; and to a paper by Prof. Poynting in Phil. Mag. vol. xlvi. p. 289 (1896), where it is shown that the dissociation hypothesis need not be pressed

too literally, that solution may be a kind of chemical combination, and yet all the facts deduced on the free ionisation hypothesis can be true. This compromise is, however, criticised by Dr. Larmor in a footnote to page 273, *op. cit.*; and Boltzmann is able to regard osmotic pressure as due to a true molecular bombardment, seeing that in the liquid state the molecular velocities should be the same as in the gaseous state at the same temperature, the mean free paths alone being smaller. On the other hand, it has been frequently claimed that any extension of gaseous laws, *i. e.* of laws deduced from the collisions of free particles, to the extremely hampered condition of a liquid, where the particles are always within each other's molecular range, must be illegitimate.

Without attempting to decide these moot points, we will here consider the question open whether the statement in terms of free ions is only a mode of expression, or whether it corresponds with the real facts; corresponds with them, that is to say, not only in result, but in actual detail. Prof. Poynting's paper, for instance, does not decide against the latter possibility, it only attempts to show that it is not really necessary to grant free ions as a physical reality; but Mr. Whetham evidently inclines to the idea that they are at least free of each other, and adduces an argument in favour of that view (pp. 233, 244, B. A. Report 1897) which is worthy of attention. But while assuming that opposite ions are free of each other, he considers that they are both attached to the solvent, and are by no means really and bombardingly free, as are the molecules of gases. Prof. Poynting appears to agree \*; but, as said above, the agreement is not universal.

The most successful application of Nernst's theory is to the calculation of the feeble E.M.F. of cells consisting of one metal but two liquids, especially when the two liquids differ only in concentration of one and the same salt.

The ideas underlying all such calculations are (*a*) that the ions migrate for two reasons: one their own random motion whereby they naturally diffuse on the average from the more concentrated to the less concentrated solution, carrying their charges with them, the other an organized motion caused by the propulsive influence on these same charges of the gradient of potential caused by their gradual diffusive accumulation; and (*b*) that in the steady state ultimately attained the rate of migration of opposite ions must become equal: otherwise the liquid would be constantly altering its composition in places.

Indeed the fact that equivalent quantities of anions and

\* Nature, 1896, vol. liv. p. 571; vol. lv. pp. 33, 78, 150, &c

cations are liberated at the electrodes, combined with the definiteness of ionic charge, shows that in electrolysis the resultant effective velocities of anion and cation substance relatively to the electrodes are equal \*.

Consider now the charged atoms or ions in a cylindrical space of volume  $Adx$ , with  $n$  of them in each unit of volume.

Let them be subject to an applied potential gradient  $dV/dx$ , and also to a self-excited osmotic pressure gradient  $dp/dx$ ; then if  $e$  is the charge on each atom, the electrical force it experiences is

$$e \frac{dV}{dx},$$

while the mechanical or osmotic force it experiences is the whole pressure difference on the element shared among the total number of atoms, which is

$$\frac{Adp}{nAdx} \quad \text{or} \quad \frac{1}{n} \frac{dp}{dx}.$$

This latter mechanical force acts equally on anions and cations, but the electrical force acts oppositely on each set; so the total force on the one set is the sum, on the other set is the difference of these two forces. If  $u_1$  and  $v_1$  are the usual migration constants representing the velocities of anion and cation respectively under unit potential gradient, their velocities under unit force will be  $u_1/e$  and  $v_1/e$ , and the actual

\* This statement seems to require a word of explanation or expansion. So much stress has been laid upon the fact of different intrinsic velocities of opposite ions when under the same conditions, that it is apt to be forgotten that in ordinary electrolysis the conditions are such as to force equal, or at least electrically equivalent velocities, on anion and cation substance taken as a whole, in the steady state. The ions are propelled not by outside forces acting from the electrodes, but by internal actions: the readjustment of the whole material must be attended to. The intrinsic speed of a projectile is greater than that of the gun-recoil, yet, after a battery has fired, the centre of gravity of the whole is no nearer the target than before. The mass-speeds are equal and opposite. In the electrical case the charge-speeds are equal and opposite. Direct experiments on specific migration velocity (such as those I described in the Brit. Assoc. Report for 1886, pp. 393, 408) are all made in purposely heterogeneous solutions; so that the motion of specific portions of matter can be discriminated and followed. Even in such heterogeneous liquids the current-strength is the same across every section; but the local potential-gradient depends on the local conductivity, and the concentration is arbitrary: it is still true, however, that the potential-gradient is the same for anion as for cation at any given place; and hence if they do ultimately travel at the same pace in spite of intrinsically different ease of travel, the fact must be expressible as due to an accumulated osmotic pressure-gradient which opposes the quicker and helps the slower.

velocities under the above forces can easily be written down. But the actual velocities in the steady state will be equal; therefore, as the condition of steadiness,

$$\frac{u_1}{e} \left( \frac{1}{n} \frac{dp}{dx} + e \frac{dV}{dx} \right) = \frac{v_1}{e} \left( \frac{1}{n} \frac{dp}{dx} - e \frac{dV}{dx} \right)$$

which simplifies to

$$ne \frac{dV}{dx} = \frac{v_1 - u_1}{v_1 + u_1} \frac{dp}{dx}.$$

At this stage it is customary to introduce the osmotic pressure gas-analogy, writing the characteristic equation of a mass  $M$  and volume  $V$ ,

$$pV = MRT,$$

where  $R$  is a characteristic constant, viz. the specific heat of expansion per gramme of perfect gas, which for hydrogen is accidentally almost equal to  $J$ , the specific heat of water.

Writing  $\frac{M}{V} = \rho = nm$ , and considering the gas pressure  $p$  to be the osmotic pressure,

$$dp = mRT dn,$$

at constant temperature.

And so finally the steady difference of potential due to diffusion between two solutions which differ only in concentration, one containing  $n$  the other  $n'$  active atoms to the litre, is

$$V - V' = \frac{m}{e} RT \frac{v_1 - u_1}{v_1 + u_1} \log \frac{n}{n'}.$$

I have written this out fully because it is usually somewhat slurred over, the electrochemical equivalent  $m/e$  omitted, the argument rendered obscure, and the dimensions wrong.

It follows that although usually the E.M.F. thus set up is very small, yet by having one of the solutions extremely weak ( $n'$  nearly = 0), the E.M.F. generated may be made surprisingly high, that is a large fraction of a volt, provided the anions and cations concerned do not diffuse at nearly the same rate under the same circumstances.

For instance, if silver is placed in a liquid containing some chloride, no molecules of silver can accumulate in any quantity in the solution, and accordingly the concentration will be almost infinitesimal, and the E.M.F. comparatively high; thus Ostwald gives the following as a cell which has, and ought on

his calculation theoretically to have, an E.M.F. of .51 or .52 volt.



the  $\text{KNO}_3$  being introduced for obvious reasons to prevent precipitation of adjacent solutions, but being without influence on the resultant E.M.F.

To calculate the total E.M.F. of a cell, however, it is necessary to take the other boundaries of the liquid into account. It is useless to complete the circuit by liquid, it must be completed by metals, and in the cases now being considered by one and the same metal. Each metal acts as a wall preventing effective diffusion of one at least of the liquid ions : the cathode prevents the cation from advancing, the anode prevents the anion ; whatever else the metals may do will be the same at each end and so balance. This is I believe the form given by Mr. Whetham to Prof. Nernst's argument.

Hence the total E.M.F. of such a cell will be the sum of the three junction-E.M.F.'s, metal/liquid, liquid/liquid, liquid/metal :

$$\begin{aligned} E &= R\epsilon T \left( \frac{(u_1 - o)}{u_1 + o} \log n + \frac{u_1 - v_1}{u_1 + v_1} \log \frac{n'}{n} + \frac{o - v_1}{o + v_1} \log n' \right) \\ &= \frac{m}{e} RT \cdot \frac{2v_1}{u_1 + v_1} \log \frac{n}{n'}. \end{aligned}$$

There is here, fortunately, no question about an innocent-looking but controversial metal/metal junction.

The remarkable thing about this equation is that the data on the right-hand side are all known, and that therefore  $E$  can be calculated in absolute measure.

Now since the characteristic gas constant  $R$ , the absolute specific heat of expansion per gram of perfect gas, varies inversely with  $m$  the atomic weight, it follows that  $Rm$  is an absolute constant, the same for every substance, or at least only differing by a simple multiple, having twice the value for electrolytic as for undissociated molecular substances ; hence we may take its value as double that for, say, hydrogen. For hydrogen  $m/e = 0.00010352$  gramme per coulomb, and  $R = 41.6 \times 10^6$  ergs per gramme degree.

Hence at  $15^\circ \text{C}$ .

$$\begin{aligned} E &= 2 \times 4.16 \times 0.00010352 \times 288 \cdot \frac{2v}{u+v} \log_e \frac{n}{n'} \text{ joules per coulomb} \\ &= \frac{.114}{1+r} \log_{10} \frac{n}{n'} \text{ volts,} \end{aligned}$$

where  $r$  is written for the Hittorfian migration ratio of anion

to cation intrinsic velocity  $u_1/v_1$ . It is remarkable that nothing is wanted except this migration ratio and the concentration ratio  $n/n'$  to calculate in absolute measure the E.M.F. of such a cell, with the same metal at either end.

A table of correspondences between theory and experiment is quoted from Ostwald and Nernst by Whetham in his B. A. Report, and they agree very remarkably indeed when one considers that the numbers are absolute numbers and might have been in error by large quantities. To illustrate this take a cell with decinormal solution of HCl on one side and centinormal solution on the other, so that the concentration ratio  $n/n' = 10$ .

For the migration ratio we might take Hittorf's own numbers (which he tabulates in the form  $u/(u+v)$  &c.) ; but several more recent and presumably more exact determinations have been made, and it may be convenient to quote here the table of absolute velocities given by Mr. Whetham as embodying the most recent measurements in 1897. As I write them they give the ionic velocity in mikroms per second for a potential gradient of 1 volt per centimetre (a mikrom being  $10^{-6}$  metre or  $10^{-4}$  cm., about double the wave-length of green light).

#### *Intrinsic Ionic Velocities.*

	$u_1$		$v_1$
Cl	6.9	K	6.6
I	6.9	Na	4.5
$\text{NO}_3$	6.4	Li	3.6
$\text{OH}$	18.2	H	32.0
$\text{C}_2\text{H}_3\text{O}_2$	3.6	$\text{NH}_4$	6.6
$\text{C}_3\text{H}_5\text{O}_2$	3.3	Ag	5.7

So for HCl the migration ratio is

$$r = \frac{6.9}{32.0} = .216,$$

and hence the theoretical E.M.F. of such a cell as that just above spoken of, with a weak solution of HCl opposed to one ten times weaker and connected by any single metal, is

$$\frac{.114}{.216} \log_{10} 10 = .0938 \text{ volt},$$

whereas Nernst gives it as observed at .0926 volt. A very remarkable agreement when we consider how the above absolute constant  $4m/eRT$ , which I have reduced to .114 volt, is constituted.

As another example take a cell containing two strengths of

$\text{NH}_4\text{Cl}$  solution with the same concentration ratio 10 : 1. In this case

$$r = \frac{69}{66} = 1.045.$$

So

$$E = \frac{.114}{2.045} = .0557 \text{ volt},$$

and Nernst gives it as observed at .0546.

Once more, take a cell filled with KOH solution 10 : 1 ;

$$r = \frac{182}{66} = 2.76,$$

therefore

$$E = \frac{.114}{3.76} = .0303 \text{ volt},$$

and it is observed at .0348.

A cell of LiCl gives another example, strength as before decinormal and centinormal, that is 1 gramme equivalent per litre on one side, and .01 ditto on the other :

$$r = \frac{69}{36} = 1.925.$$

So

$$E = \frac{.114}{2.925} = .0390 \text{ volt},$$

observed at .0354.

Here more old-fashioned values for the migration numbers give a result more nearly agreeing with observation.

Another cell where the agreement is not so close is one of caustic soda, NaOH. Nernst quotes one with strengths .235 gramme equivalents per litre on one side, and .030 on the other, so that the concentration ratio is 7.83, while the migration

ratio is  $\frac{182}{45} = 4.05$ .

The observed E.M.F. was .0178 volt, whereas the calculated is

$$\frac{.114}{5.05} \log 7.83 = .0201 \text{ volt}.$$

At least that is what I get, but as in several other cases the column of "calculated" given by Nernst does not contain the same numbers as those here obtained. Sometimes they agree with observations better, but sometimes worse.

These agreements, though not perfect, are clearly far and away beyond anything attributable to chance, and they practically substantiate the essential features of Nernst's theory, a theory which seems to me to rank high among rational

calculations of this kind. The success of this brilliant concentration theory of batteries with one metal and two liquids, or rather one liquid with different strengths, lends weight to the supplementary suggestions of the same great chemist\*, that the E.M.F. of batteries containing one liquid and two metals can likewise be calculated on similar lines. So long as the metals are the same at either side, and only the solutions have to be considered, this diffusion theory clearly represents a great step in the direction of the truth, even if it cannot be asserted at present to be the whole truth.

But when the so-called solution-pressure of a metal itself has to be taken into consideration, the ground becomes less secure and satisfactory.

When zinc dissolves in an acid this hypothesis assumes not that the zinc is eaten away by combination with the acid radical, but that it as it were evaporates into the liquid, giving rise to free zinc ions having a certain osmotic pressure.

If asked why zinc should evaporate any more freely into liquid than into air, it may be answered (as Mr. F. H. Neville suggests), because the great cohesive force, Laplace's  $K$ , would resist evaporation into air, but would be far less effective in resisting evaporation into a liquid where the change of density is much less sharply emphasised at the boundary. Hence though a certain repugnance may naturally at first be felt to this evaporation theory, it may turn out a reasonable mode of expressing facts, and it demands careful consideration.

The above mere cohesion consideration would tend, however, to make all liquids too much alike in their solvent influence on metals: the form given to the theory by Mr. Whetham and Prof. Poynting, that the ions though free of each other are chemically attached to the solvent, seems far more plausible, and overcomes many difficulties. On either view the following statements hold good.

When a metal dissolves in a liquid there is no interchange of ions, cations pass into the liquid, but no anions necessarily pass out of it. Sometimes there is an interchange of cations—one set going in and another set coming out—as when iron displaces copper, or zinc displaces hydrogen. Probably some

\* Meaning either Ostwald or Nernst. I cannot pretend to discriminate the portion belonging to each, and I hope it is not necessary. Both have done admirable work in connexion with this subject. I find that the first theory of concentration batteries, based upon thermodynamic and vapour-tension considerations of a less simple kind than those here quoted, and not depending on any ionisation hypothesis, was given by von Helmholtz in 1878 (*Wied. Ann.* vol. iii. p. 201).

impurity in the metal, enabling galvanic action to occur, is essential to this process, but that is here not a matter of primary importance.

Consider now a Daniell cell of the simplest theoretical kind :



As soon as the circuit is completed, zinc goes into solution at one end and copper comes out. The difference between the energy of combination of Zn and Cu with  $\text{SO}_4$  gives the whole E.M.F.; since, as is well known, the  $dE/dt$  and therefore the  $\Sigma(\Pi)$  happen in this case to be practically zero.

But what about the location of the E.M.F.? Leaving on one side the extraordinary contention in favour of the zinc-copper junction, there are three other junctions at which the chief portion of the E.M.F. might be located; and at first sight the liquid/liquid junction at the porous partition seems the most likely. For here it is that the actual exchange of Zn for Cu takes place; and hence it may be said, either heat must here be locally developed or else the energy must be used in propelling the electric current and developing the same quantity of heat elsewhere.

But, as Hopkinson virtually pointed out (p. 341, Phil. Mag. Oct. 1885), this involves the tacit assumption that the metallic ions do all the travelling, while the  $\text{SO}_4$  is stationary;—in that case the metallic zinc which goes into solution would at first be merely passed on, and the real energy-production would occur where zinc atoms took the place of copper atoms, viz., at the junction of solutions in the porous partition. After that there is a mere passing on again, though now of copper.

But the migration ratio of the ions is in reality different from this, and the  $\text{SO}_4$  is by no means really stationary. As another extreme assumption, suppose that the  $\text{SO}_4$  ion did all the travelling, then the zinc sulphate solution is strengthened and the copper sulphate solution is impoverished, and the whole positive energy of combination is at the surface of the zinc, while at the surface of the copper there must be a smaller opposition force corresponding to the tearing of the  $\text{SO}_4$  away from the Cu there.

Now this concentration in one compartment and weakening in the other compartment corresponds much more nearly than the first hypothesis does with what is observed, the truth being of course something intermediate between the two extremes. Anions and cations both travel, and so the total E.M.F. is shared in certain proportions between all the junctions:

a proportion which can be calculated from a knowledge of the relative rates of migration: though the observations of the true migration ratios may be complicated by molecular electric endosmose through the porous cell. Indeed, so far as I know at present, the migration velocity of  $\text{SO}_4$  has not yet been very well directly determined.

But, although all this is valid on any view as to the nature of solution, the above mode of statement belongs to the old-fashioned view of chemical combination, the notion of metallic solution which was in vogue a few years ago. It may be well to state the matter also in terms of dissociation ideas.

The fashionable method is to think of the solvent as little more than a menstrum for a stream of metallic ions to saunter through. We may think of the zinc ions travelling into the liquid and some copper ions leaving it, the adjustment of the proportion between the free zinc and the freed  $\text{SO}_4$  being a matter of subsequent diffusion. The solid zinc has, as it were, a certain vapour-tension or osmotic pressure  $P$ , the zinc of the zinc sulphate has a certain less solution-pressure  $p$ , less because it is there less concentrated than in the solid. Let there be  $N$  molecules per c.c. of solid and only  $n$  active molecules per c.c. of liquid, then the steady potential-difference between the solid and the liquid will be given by

$$\frac{dV}{dp} = \frac{1}{ne}$$

for in the present case  $\frac{v_1 - u_1}{v_1 + u_1} = 1$ , the anions being supposed stationary at that junction, since they cannot diffuse into the metal.

So putting  $p = \rho RT = nmRT$ , we get

$$dV = \frac{m}{e} \cdot RT \frac{dn}{n};$$

or

$$V - V' = ReT \log \frac{N}{n} = 114 \log_{10} \frac{N}{n} \text{ volt},$$

as the theoretical difference of potential between a metal and a solution of any one of its salts;  $e$  being written for the electrochemical equivalent  $m/e$ . Even if it is a foreign salt or an acid the potential-difference should be the same, provided there is equilibrium, *i. e.* no "local action."

Suppose now that one metal, with effective concentration  $N_1$  (active ions per c.c.), dips into a solution of concentration  $n_1$ ;

and that this solution changes abruptly to another strength  $n_2$  of the same solution, the circuit being completed by another metal  $N_2$  dipping into that second solution; then the whole E.M.F. of the cell, on the above hypothesis, is

$$\begin{aligned} E &= R\epsilon T \left( \log \frac{N_1}{n_1} + \frac{u-v}{u+v} \log \frac{n_1}{n_2} + \log \frac{n_2}{N_2} \right) \\ &= .114 \left( \log_{10} \frac{N_1}{N_2} + \frac{2v}{u+v} \log_{10} \frac{n_2}{n_1} \right) \text{ volt.} \end{aligned}$$

One case of this is the one we have already considered at length, where only one metal is employed, that is, where  $N_1 = N_2$ , and the E.M.F. depends wholly on the solutions. The other chief case is the ordinary simple Volta cell, where  $n_2 = n_1$ , and where the theoretical E.M.F. depends solely on the two metals.

But now suppose that the two liquids are different, as well as the two metals; there will now be altogether four ionic velocities and four real or virtual concentrations:—

$$u_1, v_1; \quad u_2, v_2; \quad n_1, n_2; \quad N_1, N_2$$

So assuming that each solution acts like vacuum to the other, we have intrinsic velocities  $u_1$  out and  $v_2$  in across the liquid boundary of the first solution, or an E.M.F. at that place of

$$\cdot114 \frac{u_1 - v_2}{u_1 + v_2} \log n_1 \text{ volt;} \quad (1)$$

together with

$$\cdot114 \frac{v_1 - u_2}{v_1 + u_2} \log n_2 \text{ volt} \quad (2)$$

to be added to it, for the same boundary, considered from the point of view of the other solution.

Hence in this case, with two different metals,

$$\frac{E}{\cdot114 \text{ volt}} = \log_{10} \frac{N_1}{N_2} - \frac{2v_2}{u_1 + v_2} \log_{10} n_1 + \frac{2v_1}{u_2 + v_1} \log_{10} n_2.$$

And the first term is usually the most important. For the special case where  $\frac{v_2}{u_1} = \frac{v_1}{u_2} = \frac{1}{r}$ , the two last terms reduce to the simple concentration expression already familiar,  $\frac{2}{1+r} \log \frac{n_2}{n_1}$ . The osmotic pressure ratio  $n_2/n_1$  for the liquids may be a measure of their relative conductivities; but the solution-pressure ratio  $N_1/N_2$  for the metals seems to be

exponentially connected with their chemical activity, *e. g.* their heat of oxidation.

It is needless to point out that in the above equation most voltaic cells are included, at least if one is content to omit from consideration the inert non-migrational non-chemical junction of the two metals.

Some remarkable cells of this kind have been suggested where the liquids overpower the metals, so to speak; none more so than a cell specified by Hittorf \*, who says that by surrounding copper with a solution of a cyanide it can be made electropositive to zinc, so that copper shall go into solution and zinc shall be turned out, being deposited upon a zinc plate.

The scheme for this cell of Hittorf's is said to be



The object of the  $\text{K}_2\text{SO}_4$  is, as in many of these cells, to interpose a neutral harmless substance between two solutions which otherwise would precipitate each other.

Perhaps some one will set up a cell of this kind and verify the statement; though Hittorf's is very high authority.

#### *Electron or Corpuscular View of Voltaic Action.*

The theory which seeks to reduce the whole material universe to electric charges, their motions and interactions, constitutes a gigantic subject upon which it is scarcely rash to predict that a great deal will be said during the ensuing century.

Dr. Larmor (*Phil. Trans.*) seeks not only to explain physical phenomena in general by means of electrons, but also to explain the electron itself as an intrinsic æther strain. Prof. J. J. Thomson (*Phil. Mag. passim*, especially December 1899) adduces experimental facts in favour of the real and even isolated existence of such charged corpuscles, whether they be pure electrons or not.

Meanwhile the mode of expression in term of corpuscles is less ambitious than that in terms of electrons, though both are revolutionary and striking enough. Let us take it then as granted hypothetically that every material atom is built up of the same fundamental corpuscles, each with the usual ionic charge; a hydrogen atom being composed of about 500 of such corpuscles of opposite signs, a sodium atom of about 10,000, and a mercury atom of about 100,000 of them.

Let every electric current (except a displacement current in

\* *Zeits. f. physical. Chem.* 1892, vol. x. p. 592.

free space) be associated with a transfer of corpuscles, a convection of ionic charges, whether in liquids or in metals or in gases ; the only difference being that in liquids the travelling corpuscle carries the whole atom with it, whereas in gases it can travel in some cases isolated from all the rest of an atom\*, though in other cases it may be clogged with a considerable molecular aggregate of atoms †; while in solids presumably a corpuscle can only travel by being handed on from one atom to the next : though a shift inside each atom will correspond to a polarisation current.

At an electrode the corpuscle leaves its ion to do the best it can, and passes on into the metal, each atom receiving it into its atomic grouping and instantaneously passing on an equal corpuscle to the next : or at least that is what I suppose to happen, consistently with the hypothesis. At a junction of two metals, then, a corpuscle which had formed part of an atom of one metal finds itself received and incorporated by a different kind of atom. This may clearly involve a gain or a loss of energy, and accordingly some propelling or opposing E.M.F. It may be expressed if we choose somewhat in the language of Helmholtz's hypothesis, that one metal attracts electricity more forcibly than another. If the excess energy takes the form of molecular agitation, such a procedure may entirely account for the Peltier and Seebeck phenomena.

I have spoken of it above (April, p. 364) as a futile kind of "transmutation" : "transmutation" because a portion of the substance of say an iron atom enters into and becomes part of the substance of a copper atom ; "futile" because there is no effective conversion of iron into copper, since the amount of each metal remains the same as before.

If corpuscles could be passed into a metal without being passed out again there would be a kind of transmutation, and this is hypothetically done when a body is charged with negative electricity ; it has gained corpuscles which do not belong to it. But the fact that they do not belong to it—being evidently there on sufferance and tending to escape as soon as possible—shows that there is no real transmutation : a charged sodium atom is not a mere sodium atom but a sodium monad ion ; it has one negative corpuscle too many.

It might be thought that by giving to a metal charges of positive and negative electricity alternately some extra atoms could be built up : but unfortunately this is not consistent with the fact that, under known circumstances, the negatively

\* J. J. Thomson, Phil. Mag. Dec. 1899.

† Cf. Chattock, Phil. Mag. Nov. 1899 ; also Rutherford, Townsend, Wilson, &c., Phil. Trans.

charged corpuscle is the mobile ingredient; so that superposing a positive charge on a negatively charged atom is not adding something to the corpuscles already there, but is removing the extra negative corpuscle and another as well; taking the atom down therefore instead of building it up, and leaving a void which automatically fills itself up whenever it gets a chance. It is just possible that some kind of effective transmutation might be effected in an electric spark or arc with different materials on either side of it; like a substance passing over from one crystalline form to another.

Whether combination of atoms takes place across any junction when a current passes, appears to be merely a question of relative mobility of corpuscles and atoms. If the atoms are free to move, if it is easier to move an atom across the interface than to detach from it a corpuscle, then combination occurs, and the conduction is then necessarily on one side essentially electrolytic; and at a liquid-liquid junction there may be double atomic freedom and complete electrolysis. But if the corpuscles are more detachable than the atoms, then the conduction is metallic and no alloy is formed.

But now, pressing further the osmotic pressure view, if the metals can evaporate into a liquid they ought perhaps to be able to evaporate into each other, and so the E.M.F. at a junction ought to be calculable as

$$E = R\epsilon T \left( \frac{n}{n'} \right) \log \frac{n}{n'}$$

where the  $\frac{n}{n'}$  may be taken as the ratio of the metallic densities; but what shall we put into the brackets for the ionic velocities? Not ionic velocities at all, but corpuscular velocities, and these corpuscular velocities may differ by reason of the different viscosity or obstruction offered by each metal; which again perhaps may be proportional to the density; but the solution can hardly be treated as a weak one, or the gaseous laws as applicable.

If gaseous laws are applicable to the corpuscles inside metal, the value of this characteristic constant  $R$  will be 500 or 600 times the value for hydrogen; but inasmuch as the  $m$ , or  $\epsilon$  the electrochemical equivalent, is 1/500 or 1/600 of the hydrogen value, the resulting  $R\epsilon T$  comes out just as usual.

The viscosity or obstruction offered by metal is probably its electrical resistance; and so the corpuscular velocity in each may be proportional to the conductivity.

Conductivity in a liquid means greater mobility of the

ions, conductivity in a metal may mean greater mobility of the corpuscles; hence perhaps the E.M.F. of a metallic junction might be something like this :

$$E = \cdot114 \frac{k - k'}{k + k'} \log \frac{m/\rho}{m'/\rho'} \text{ volt},$$

where the  $k$  are conductivities and the  $m$  atomic weights and the  $\rho$  densities.

I would suggest that the curious deterioration suffered by some thermo-electric piles with lapse of time, especially those used for generating a fair amount of power, has never so far as I know attracted much attention or been thoroughly investigated. It may be merely mechanical, due to alternate heating and cooling, but it may possibly be due to something of greater interest.

The corpuscles clinging to atoms are rather like ions clinging to solvent; so perhaps in a metal the negative corpuscles move with velocity

$$u = u_1 \left( \frac{1}{Ne} \frac{dp}{dx} + \frac{dV}{dx} \right)$$

where the intrinsic velocity  $u_1$  is large, while the positive corpuscles move with velocity

$$v = v_1 \left( \frac{1}{Ne} \frac{dp}{dx} - \frac{dV}{dx} \right),$$

their intrinsic velocity  $v_1$  being very small.

But in a homogeneous metal itself these speeds  $u$  and  $v$  are perhaps equal; indeed where there is no potential gradient or driven current they must be equal.

Are they equal at a metallic junction too?, or is anything kinetic occurring there at all?

There must be a stress or polarisation or double layer or something statical at such a junction; and a statical condition can be simulated by kinetic equilibrium. What are the arguments?

When a zinc surface is illuminated with ultra-violet light J. J. Thomson found that it does not throw off corpuscles unless it is negatively electrified. The ultra-violet light may be said to detach them, but it takes electrification to throw them off.

So at a junction of two metals when no current is being passed it may be that there is no interchange of substance; but the interchange may or must begin as soon as a current flows; and if the A aggregation has more potential energy

then the B aggregation there will be a force urging the corpuscles to flow from A to B.

In a gas the negative corpuscles are by far the most mobile ; indeed the positive corpuscles seem unable to move except with their atoms electrolytically. It may be that even inside a metal the negative corpuscles are likewise by far the most mobile, being readily handed on from one atom to the next, this process constituting metallic conduction ; while the positive corpuscles remain attached to their atoms, which except in an electrolyte or a substance with some electrolytic properties are not subject to locomotion at all. Assuming this mobility of corpuscles of one sign solely, they are urged along a gradient of temperature in a metal for two reasons : one a mechanical force equivalent to a  $dp/dx$  acting on an element of volume, or  $1/n$  of this per corpuscle ; the other an electrical force  $dV/dx$  acting on its electric charge  $e$ .

When there is no current these forces must balance. So

$$\frac{1}{n} \frac{dp}{dx} - e \frac{dV}{dx} = 0,$$

or

$$dp = nedV.$$

Now proceeding as usual without compunction to utilise the gas-analogy

$$p = nmRT,$$

we have

$$nedV = mRd(nT).$$

or

$$dV = m/e \cdot RT d \log (nT).$$

This is the E.M.F. that acts along the gradient of temperature, giving rise to a reversible evolution of heat and representing the coefficient of the Thomson effect,  $\sigma$ , called the specific heat of electricity in a metal, such that the work done in transferring a charge  $q$  up a difference of temperature  $dT$  is  $qdV = q\sigma dT$ , or

$$\sigma = \frac{m}{e} RT \frac{d}{dT} \log (nT).$$

Hence for a circuit of two metals  $a$  and  $b$

$$\sigma_a - \sigma_b = R\epsilon T \frac{d}{dT} \log \frac{n_a}{n_b}.$$

And by ordinary thermodynamics this is related to the Peltier effect at the junction and to the resultant E.M.F. in

the circuit by the equations

$$\int \frac{\sigma_a - \sigma_b}{T} dT = \frac{dE}{dT} = \frac{\Pi}{T};$$

therefore

$$\Pi = R\epsilon T \log \frac{n_a}{n_b}.$$

Now  $n$  represents the number of active corpuscles in unit volume, and this number is a function of the temperature; and its rate of change probably depends on the number already there and on a coefficient characteristic of the metal;  $\frac{dn}{n} = \alpha dT$ , say; therefore let  $n_a = a e^{\alpha T}$ ,  $n_b = b e^{\beta T}$ .

In substances whose conductivity increases with temperature  $\alpha$  will be positive, but in metals it is usually negative; and at absolute zero the conductivity would rise to a maximum value corresponding to the maximum corpuscular concentration  $a$  or  $b$ .

So

$$\Pi = R\epsilon T \log \frac{a}{b} + (\alpha - \beta) R\epsilon T^2;$$

whence the neutral point is

$$T_0 = \frac{\log b - \log a}{\alpha - \beta},$$

and

$$\sigma_a = \alpha R\epsilon T = k_a T,$$

and

$$\Theta_a = \frac{1}{2} \alpha R\epsilon (T_1^2 - T_2^2),$$

and

$$E = (\alpha - \beta) R\epsilon (T_1 - T_2)(T_0 - \frac{1}{2}(T_1 + T_2)),$$

or

$$P_a = \alpha R\epsilon (T_0 - \bar{T}).$$

So that hypothesis does fairly well to express thermoelectric facts; but, unless the opposite sign of corpuscles is attended to, it does not account for the fact that the coefficient  $\sigma$  is positive in some metals and negative in others; though it suggests an opposite sign for  $\sigma$  in metals and electrolytes, because  $\alpha$  changes sign along with the temperature-coefficient of conductivity.

To divide metals into two classes we must not suppose that the negative corpuscles do all the travelling: if they did, moreover, the Hall effect, the magnetic influence on the current, corresponding to the magnetic curvature of cathode rays, would be much greater than it is. The facts that the Hall effect is small, and that it has different signs in

different metals, suggest, as J. Larmor points out, that the speed of the negative and positive corpuscles or electrons is nearly equal, but that in some metals the positive travel slightly faster, in other metals the negative : the difference being subordinate and secondary.

It will turn out on this view that the "specific heat of electricity"  $\sigma$ , the coefficient of the Thomson effect, has the same sign as the coefficient of magnetic curvature of current, the Hall effect. For proceed with our theory of metallic conduction treated as a convection of charged corpuscles of both kinds, with  $u/v$  the Hittorfian migration ratio of negative to positive corpuscular velocity, under the action of unit force; and write down as in electrolysis that the resultant motion must be equal in opposite directions,

$$u \left( \frac{1}{n} \frac{dp}{dx} + e \frac{dV}{dx} \right) = v \left( \frac{1}{n} \frac{dp}{dx} - e \frac{dV}{dx} \right),$$

or

$$\frac{dV}{dp} = \frac{1}{ne} \frac{u-v}{u+v},$$

or

$$dp = ne \frac{u+v}{u-v} dV.$$

Then the various thermoelectric quantities get written exactly as above, except that the new factor  $\frac{u-v}{u+v}$  must be everywhere introduced.

It is worth noticing that

$$ne(u+v) = \frac{C/A}{nV/dx} = \frac{\text{current-density}}{\text{potential-gradient}} = \text{specific conductivity} = \frac{1}{\rho};$$

wherefore

$$\begin{aligned} \sigma &= \frac{dV}{dT} = \rho(u-v) \frac{dp}{dT} \\ &= \rho m R(u-v) \frac{d}{dT}(nT). \end{aligned}$$

This form is instructive as showing that, other things being equal, highly resisting substances are likely to form the best thermoelectric materials. The metals of high conductivity have, in fact, feeble thermoelectric power; metals like bismuth and antimony are poor conductors; and the contact force between insulators, or still better between an insulator and a conductor, may be enormous.

But for most purposes the previous form of expression is

handier, so introducing the migration ratio  $r = u/v$  we get

$$\sigma = R\epsilon T \frac{1-r}{1+r} \frac{d \log (nT)}{dT};$$

and so on for II and E as before when two metals are employed, only with the new relative migration factor which permits ready change of sign; and it must be remembered that the corpuscular migration ratio  $r$ , as well as the corpuscular detachment number  $n$ , may differ in the two metals.

#### *Helmholtz's View of Electric Mass-Affinity.*

The doctrine that matter has a specific attraction for electricity \* leads to many of the same conclusions as the supposition that positive or negative electricity inside a substance has a real specific heat, and the two modes of statement may be considered together; but we may speak in the language of Helmholtz's hypothesis as being the more important of the two, indeed the only one seriously upheld as a physical reality. As has been suggested above, p. 369, it is to some extent ambiguous, however; for it is not certain whether the affinity or attraction is effective at a metal-aether free surface or at a metal-metal junction. As usually stated, the attraction is supposed to be an affair of mass or bulk and not of surface, though no doubt any such internal volume electric stress would give rise to something analogous to electrical surface-tension; but the whole may be really and essentially superficial, having to do with the free surface only; and in that case it is difficult to distinguish it from chemical affinity, unless it can truly be shown to be independent of the presence and nature of surrounding adjacent matter. Even so it may be considered as an early and crude statement of certain consequences of the electron theory of matter, rather than as a distinct and independent theory (*cf.* J. Larmor, Phil. Trans. 1897, vol. exc. p. 271).

However it be regarded, it is plain that the effect of an attraction between matter and electricity must display itself at a transition or boundary layer, and although it has been customary to concentrate attention on the metallic (*e.g.* the copper-zinc) junction in this connexion, it is by no means probable that that is so efficient or complete a transition as the free air or aether surface of either metal; nevertheless these surface actions have secured too little attention.

The proofs that have been given, for instance, of the value of the Peltier effect, and its connexion with contact force,

\* For references see Phil. Mag. October 1885, p. 377.

or boundary force as we might now call it, are accustomed more or less completely to ignore the air boundaries ; employing an open circuit with the object of avoiding obvious neutralising or compensating forces at other junctions, but forgetting that opening a circuit necessarily introduces one *more* boundary, not one *less*.

Dr. Larmor has been good enough to tell me of a "proof" in Parker's 'Thermodynamics' (1894 edition) that on Helmholtz's view the Peltier coefficient at a metallic junction is proportional to the rate of change of the junction force there with temperature ; a proof somewhat on the same lines as that given independently by Lord Kelvin in the Proc. Roy. Soc. Edin. vol. xxii. page 118, Session 1897-8 ; but neither proof in reality establishes anything specially limited to the metallic junction ; the whole of the junctions are really laid under contribution, a fact which is half recognised by Lord Kelvin, though not by Mr. Parker.

In order to save other people from working through these proofs I may reword them in a simpler and briefer fashion, using language appropriate to the mass-affinity doctrine, but incidentally throwing in the symbol  $\sigma$  so as to include also the essence of the specific heat idea.

Let a charge of electricity given to a metal be held there by an intrinsic attraction or mass-affinity ; it will have a special affinity-energy in addition to the energy of its ordinary electrical interactions with other charges : call this surplus energy, at the absolute temperature  $\theta$ ,

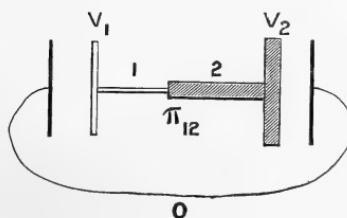
$$u = u_0 + \int \sigma d\theta.$$

The corresponding entropy is

$$s = s_0 + \int \frac{\sigma d\theta}{\theta} = s_0 + \int \frac{du}{\theta},$$

so that

$$du = \sigma d\theta = \theta ds.$$



Consider an open circuit of two active metals and one neutral substance, *e.g.* Zn, Cu, and Pt, or 1, 2, and 0, with air-gaps forming condensers as in the diagram ; the condensers being

charged to the potentials  $V_1$  and  $V_2$  respectively by the differential electric affinities at work.

Now transfer unit charge reversibly from one condenser to the other, *i.e.* from potential  $V_1$  to  $V_2$ , by shifting the neutral plates ; the work done, equivalent to loss of energy, has usually been written as

$$V_2 - V_1 = \Pi_{12} + u_1 - u_2,$$

but it ought to be written

$$V_2 - V_1 = \Pi_{01} + u_1 + \Pi_{12} - u_2 + \Pi_{20}.$$

The total entropy change is zero,

$$\frac{\Sigma \Pi}{\theta} + s_1 - s_2 = 0,$$

or, writing  $\Pi$  for  $\Sigma(\Pi)$ ,

$$\Pi = \theta(s_2 - s_1),$$

wherfore

$$V_2 - V_1 = u_1 - u_2 - \theta(s_1 - s_2),$$

or

$$V + u - \theta s = \text{constant}.$$

But

$$u - u_0 = \int \theta ds = \theta s - \int s d\theta,$$

so

$$V - \int s d\theta = \text{constant},$$

or

$$\frac{dV}{d\theta} = s,$$

or

$$\frac{\Pi}{\theta} = s_2 - s_1 = \frac{d}{d\theta}(V_2 - V_1);$$

the result to be proved.

But there is nothing here more than has been admitted in this paper over and over again.

If surface boundary forces are supposed zero, if electricity can enter or leave the free surface of a metal without aid or obstruction, then  $V_1 - V_2$  must represent the only remaining force, viz. that at the metallic junction ; and the only  $\Pi$  will be situated there ; but if there are other boundary forces then  $V_1 - V_2$  represents the whole E.M.F. of the circuit, and not the localised junction force at all, and  $\Pi_{12}$  is not necessarily the sole Peltier effect. The metallic junction force may still be measured by  $\Pi_{12}$  ; the combined entropy of the boundary

forces is  $\Sigma \Pi / \theta$ ; and this entropy is proved equal to  $dE/d\theta$ , a remarkable and interesting but long known fact.

Returning to the theory of Helmholtz, which was stated first so long ago as 1847, and elaborated to some extent in his brilliant "Faraday lecture" of 1881, it is undoubtedly very important; it may be regarded as the precursor of, and therefore to some extent superseded by, the electron or corpuscular theory of matter: a theory which represents the natural outcome, in the light of recent experiments, of that "atomic" view of electricity which, started by Clerk Maxwell in an inspired phrase, adopted and expanded by Dr. Johnstone Stoney and others, is now in the preceding pages attempted to be applied, in conjunction with ideas derived from the treatment of osmotic pressure by physical chemists, to an explanation of thermoelectric action on the gaseous analogy.

[To be continued.]

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**XLIV. *On certain supposed Irreversible Processes.***

*By S. H. BURBURY, F.R.S.\**

1. CERTAIN processes in nature are irreversible. If for instance mechanical energy be converted into heat, only a part of it can, as a net result, be reconverted. The energy, or part of it, is dissipated.

2. We are taught in the kinetic theory of gases that heat consists of, or is proportional to, the energy of molecular motions in the stationary state which involve no dissipation of energy, and are therefore reversible. If this theory be true, there should exist processes which, as they relate to an aggregate of molecules, are irreversible, although they consist of molecular motions each separately reversible. Can any such process be proved to exist?

3. The analytical theorems which are supposed to prove the existence of such processes have generally the following form. It is proved that a function, always of the same sign, diminishes or increases until a limit is reached, which limit may be a maximum or minimum for the function in question, and when that limit is reached the motion is stationary. Any such function may be called the *characteristic function* of the process in question, and shall be denoted by  $H$ .

It is sufficient to consider the case where  $H$  is a diminishing

\* Communicated by the Author.

function and  $\frac{dH}{dt}$  negative. It does not matter, as regards the question of reversibility, whether  $\frac{dH}{dt}$  is necessarily negative, or only more likely at each stage of the process to be negative than to be positive. It is enough if a distinction exists between the *forward* motion in which  $\frac{dH}{dt}$  is negative, and the *backward* motion in which  $\frac{dH}{dt}$  is positive. In this distinction consists the irreversibility. But the distinction must exist at every stage of the process at which  $H$  exceeds its minimum.

4. The best known of these theorems is Boltzmann's  $H$  theorem in the theory of gases, wherein it is proved that his function  $H$  continually diminishes till a certain state is reached, which involves the equal partition of energy.

So Herr Planck in his treatise *über irreversible Strahlungsvorgänge* proves that a function  $L$ , the entropy of his system, necessarily increases till a state is reached analogous to the equal partition of energy. But in Planck's theorem we have to do, not with molecular motions each evidently reversible, but with electromagnetic vibrations in æther, about which we cannot say with the same certainty that they are reversible separately. At present I propose to deal only with Boltzmann's theorem, as a type of theorems founded on molecular motions certainly reversible.

#### *The Directing Condition.*

5. All the molecular motions being reversible, the fact that  $H > H_0$  cannot alone make  $\frac{dH}{dt}$  negative. For we may reverse all the velocities, and that reversal in continuous motion changes the sign of  $\frac{dH}{dt}$  without altering the value of  $H - H_0$ . Some further condition is therefore required to determine the sign of  $\frac{dH}{dt}$ . This we may call the *directing condition*.

6. The directing condition being defined, there arises the question whether or not it exists in fact. If it does, the diminution of  $H$  is an irreversible process. If not, the process is not proved to be irreversible. Boltzmann's condition in his Theory of Gases is that the motion is, and continues to be, "molecular ungeordnet." That, if it can be defined, may be the most general form of the condition. For my present

theoretical purpose it is sufficient to deal with the test-case of elastic spheres, and for that case the condition may be expressed as follows :—The chance that two spheres *approaching collision* shall have velocities within assigned limits is independent of their relative position, and of the positions and velocities of all other spheres, and also independent of the past history of the system, except as this has altered the distribution of the velocities *inter se*.

This condition of independence is, as I propose to show, the directing condition required to make the diminution of  $H$  in the test-case an irreversible process. I propose also to consider as far as possible whether this directing condition can be assumed to exist in fact.

7. Let us first take an algebraic example. There are in a bag  $n$  white and  $n'$  black balls. I draw at random  $r$  balls,  $r$  being small compared with  $n$  or  $n'$ , and they happen to be  $p$  white and  $q$  black, with  $p+q=r$ . I then return to the bag, not  $p$  white and  $q$  black which I drew, but  $q$  white and  $p$  black, so that as the result of the drawing and return,  $n$  has become  $n+q-p$ , and  $n'$  has become  $n'+p-q$ ;  $n+n'$  is unchanged, but  $n-n'$  has become  $n-n'+2(q-p)$ . Now, on average, the most probable values of  $p$  and  $q$  are

$$p = \frac{n}{n+n'} r, \quad q = \frac{n'}{n+n'} r;$$

so the effect of the drawing and return is on average to diminish the difference  $n-n'$ . And if the process be repeated indefinitely,  $n-n'$  will, on the whole, diminish. But at any drawing the actual values of  $p$  and  $q$  will generally differ from their mean values. We may express this by saying that the actual value of  $p$  is  $\frac{k}{n+n'} n$ , where  $k$  is a positive quantity, not greater than  $\frac{n+n'}{n}$ , whose mean value is unity and which is more likely to have a value nearer to unity than one more remote. Then

$$q=r-p=\frac{n'+(1-k)n}{n+n'} r, \text{ and } (q-p)=\frac{n'+(1-2k)n}{n+n'} r.$$

To give a concrete example, let  $r=100$ . Let  $P$  be the chance that  $p-q=2$ , and  $P'$  the chance that  $q-p=2$ . Then approximately

$$P/P' = \left(\frac{n}{n'}\right),$$

which is very great if  $n/n'$  is great, but approaches unity as  $n/n'$  approaches unity.

We have here an irreversible process. We might take  $n' \sim n$  for characteristic function, but for symmetry let

$$H = n \log n - n + n' \log n' - n',$$

and let  $\partial n$  or  $\partial n'$  denote the change of  $n$  or  $n'$  due to one drawing and return. Then  $\partial n = (q-p)r$  and

$$\begin{aligned}\partial H &= \log n \partial n + \log n' \partial n' \\ &= \partial n \log \frac{n}{n'}, \text{ because } \partial(n+n')=0, \\ &= \frac{n'+(1-2k)n}{n+n'} r \log \frac{n}{n'} \\ &= \frac{n'-n}{n+n'} r \log \frac{n}{n'}, \text{ on average.}\end{aligned}$$

And this is negative or zero.  $H$  is the *characteristic function* of the process. The *directing condition* is that each drawing is at random, and independent of the past history of the system, that is independent of all former drawings, except as they have altered  $n$  and  $n'$ .

#### *Equal Elastic Spheres.*

8. A great number of elastic spheres, each of unit mass and diameter  $a$ , are at an initial instant set in motion within a field of no force  $S$  bounded by elastic walls. The initial motion is formed as follows:—(1) One person assigns component velocities  $u, v, w$  to each sphere according to any law subject to the condition that  $\Sigma u = \Sigma v = \Sigma w = 0$  and  $\Sigma(u^2 + v^2 + w^2) = \text{a given constant}$ . (2) Another person, in complete ignorance of the velocities so assigned, scatters the spheres at haphazard throughout  $S$ . And they start from the initial positions so assigned by (2) with the velocities assigned to them respectively by (1).

The condition of independence of Art. 6 is evidently satisfied in this initial state.

9. Let  $f du dv dw$  be the number of spheres having in the initial distribution (1) component velocities between the limits

$$\begin{aligned}u &\dots u+du, \\ v &\dots v+dv, \\ w &\dots w+dw.\end{aligned}$$

These we will call  $f$  spheres, or spheres of the class  $f$ . And let  $F dU dV dW$  be the number having in the initial distri-

bution (1) component velocities between the limits

$$\begin{aligned} U &\dots U + dU, \\ V &\dots V + dV, \\ W &\dots W + dW. \end{aligned}$$

There we will call F spheres, or spheres of the class F. The relative velocity, R, of any f with any F has components  $u - U, v - V, w - W$ . The number of pairs, each containing an f and an F, is  $fF du dv dw dU dV dW$ , or shortly  $fF d\sigma$ .

10. Now adjacent to every f sphere construct an element of volume thus:—About its centre describe a spherical surface of radius a (the diameter of a sphere). And the direction of R being polar axis, let  $\theta, \phi$  be the usual coordinates defining a point on that surface. Then the element of volume shall be

$$a^2 \sin \theta \cos \theta d\theta d\phi R dt = d\eta dt.$$

It may be on either side of the f sphere according as  $\theta >$  or  $< \frac{\pi}{2}$ . And it shall be so taken that an F sphere whose centre is within  $d\eta dt$  is approaching the f sphere.

If we neglect the rare cases in which one such element contains the centre of more than one F sphere, the number of these elements which contain an F sphere is, on average,

$$fF d\sigma d\eta dt.$$

Its actual value at the initial instant will generally differ from this average, because it depends on the chance distribution (2). Let this actual value be

$$kfF d\sigma d\eta dt,$$

where k is a positive quantity whose mean value is unity, and for which a value nearer to unity is more probable than one more remote.

11. Every one of these F spheres whose centre is within one of the elements  $d\eta dt$  will within the time  $dt$  after the initial instant collide with the f sphere to which the element belongs. We here neglect, as we may, the chance that one of the two spheres whose collision with each other is arranged may disappoint its partner by previously colliding with some third sphere. The actual number of such collisions in the time  $dt$  is therefore  $kfF d\sigma d\eta dt$ , and its average value is  $fF d\sigma d\eta dt$ .

Each of these collisions diminishes the number of the class f by one.

12. After collision the  $f$  sphere will have component velocities

$$\begin{aligned} u' & \quad . \quad . \quad . \quad u' + du', \\ v' & \quad . \quad . \quad . \quad v' + dv', \\ w' & \quad . \quad . \quad . \quad w' + dw', \end{aligned}$$

that is will have passed into the class  $f'$ , and the F sphere will have component velocities

$$\begin{aligned} U' & \quad . \quad . \quad . \quad U' + dU', \\ V' & \quad . \quad . \quad . \quad V' + dV', \\ W' & \quad . \quad . \quad . \quad W' + dW', \end{aligned}$$

that is will have passed into the class  $F'$ . Now

$u'^2 + v'^2 + w'^2 + U'^2 + V'^2 + W'^2 = u^2 + v^2 + w^2 + U^2 + V^2 + W^2$ , and

$$u'U' + v'V' + w'W' = uU + vV + wW.$$

Also  $\theta \phi$  remain unchanged, and R is unchanged in magnitude, but its components are now

$$u' - U', \quad v' - V', \quad w' - W'.$$

Also by a known theorem

$$du' dv' dw' dU' dV' dW' = du dv dw dU dV dW.$$

13. Exactly in the same way, if about every sphere which initially in the distribution (1) belongs to the class  $f'$ , we describe an element of volume with the same  $\theta$  and  $\phi$  as before, but with the new direction of R for axis, every  $F'$  sphere which is initially within one of these elements will within the time  $dt$  after the initial instant collide with the  $f'$  sphere to which the element belongs, and after collision  $f'$  and  $F'$  will have passed into the classes  $f$  and  $F$  respectively. The number of such reverse collisions in the time  $dt$  is actually

$$k'f'F' du' dv' dw' dU' dV' dW' a^2 \sin \theta \cos \theta d\theta d\phi R dt,$$

or, which is the same thing,

$$k'f'F' du dv dw dU dV dW a^2 \sin \theta \cos \theta d\theta d\phi R dt,$$

that is  $k'f'F' d\sigma d\eta dt$ , and its mean value is  $f'F' d\sigma d\eta dt$ . Here  $k' = 1$  on average, as  $k = 1$ , but  $k'$  is independent of  $k$ .

14. Every collision of this second kind increases the number of the class  $f$  by one. It follows that, taking into consideration all collisions,

$$\frac{df}{dt} = \iiint (k'f'F' - kfF) dU dV dW \iint a^2 \sin \theta \cos \theta d\theta d\phi R.$$

That is the actual value. The mean value is

$$\frac{df}{dt} = \iiint (f'F' - fF) dU dV dW \iint a^2 \sin \theta \cos \theta d\theta d\phi R.$$

These values of  $\frac{df}{dt}$  relate to the initial instant, and an interval  $dt$  after it.

15. Now let us consider the difference between the two expressions  $(k'f'F' - kfF)$ , which is the actual, and  $(f'F' - fF)$  which is the mean value. It is possible that  $k'f'F' - kfF$  may be of the opposite sign to  $f'F' - fF$ , but the greater the absolute value of the difference  $f'F' - fF$ , or the ratio of that difference to  $f'F' + fF$ , the less probable it is that  $k'f'F' - kfF$  shall be of the opposite sign to  $f'F' - fF$ .

*Boltzmann's H Theorem.*

16. Still considering the system in its initial state, let

$$H = \iiint_{-\infty}^{+\infty} du dv dw f(\log f - 1).$$

Then

$$\begin{aligned} \frac{dH}{dt} &= \iiint_{-\infty}^{+\infty} du dv dw \frac{df}{dt} \log f \\ &= \pi a^2 \iiint_{-\infty}^{+\infty} du dv dw dU dV dW (k'F'f' - kfF) R \log \frac{fF}{f'F'} \end{aligned}$$

by a known process. And on average, writing  $K' = K = 1$ ,

$$\frac{dH}{dt} = \pi a^2 \iiint_{-\infty}^{+\infty} du dv dw dU dV dW (F'f' - Ff) R \log \frac{fF}{F'f'},$$

which is necessarily negative if not zero. It will be noted that the logarithmic factors are not affected by the coefficients  $k$  and  $k'$ .

17. It is evident from the foregoing that  $\frac{dH}{dt}$  may be positive, if, namely, many of the factors  $k'F'f' - kfF$  differ in sign from their mean values  $F'f' - Ff$ . And it is further evident that the chance of  $\frac{dH}{dt}$  being positive is greater as the factors  $F'f' - Ff$  are in absolute value less.

18. The reasoning is based on the assumption, which in the initial state is true, that the chance of two spheres being in the classes  $f$  and  $F$  is independent of their relative positions. It is also independent of the past history of the system, because, as we have formed it, the system has no past. If the results are to hold for every subsequent state of the systems the condition of independence must also hold. But if no

external disturbance happens to the system, the positions and velocities of all the spheres at any time  $t$  are determinate functions of  $t$  and the initial positions and velocities, and of no other quantity whatever. The condition of independence cannot therefore strictly hold for all time, though it may hold approximately. For any two of the velocities, as  $u$  and  $u'$ , are functions of the same set of variables. It cannot therefore be assumed at least without further investigation that they are independent of one another.

19. In order therefore to maintain the condition of independence without doubt, let us assume that after the lapse of time  $dt$ , and again after every subsequent interval  $dt$ , some external cause, say Maxwell's demons, effects a redistribution of the positions of the spheres without altering any of their velocities. And this is done in such a way as always to maintain the independence.

20. Since on this assumption the independence exists at every instant, the same reasoning may be applied at any subsequent instant which we applied at the initial instant. Then  $\frac{dH}{dt}$  is at every instant on average zero or negative. If the demons, in addition to their other services, would insure that  $\frac{df}{dt}$  should always have its mean value in which  $k=k'=1$ ,  $H$  would continuously diminish. In fact,  $\frac{dH}{dt}$  may, as we have seen, be occasionally positive. But as long as many of the factors  $F'f' \sim Ff$  have a great value, it is very improbable that  $\frac{dH}{dt}$  should be positive. The diminution of  $H$ , and also the diminution of every  $F'f' \sim Ff$ , will therefore go on with little interruption until every  $F'f' - Ff$  is very nearly zero, and  $H$  nearly minimum. But when this state is attained,  $\frac{dH}{dt}$  is nearly as likely to be positive as to be negative.

21. Now, the condition of independence being maintained, let us consider the chance that  $H$ , having attained its minimum  $H_0$  at time  $t$ , shall subsequently again increase and, say at time  $t+t'$ , attain a value  $H'$ , considerably greater than  $H_0$ . We may suppose the time  $t'$  to be divided into  $n$  intervals each equal to  $d\tau$ . Let  $P_r$  be the chance that in the  $r$ th interval  $H$  shall receive the increment  $d_r H$ . Then, by the condition of independence assumed to exist, the chance that  $H$  shall during the time  $t'$  increase from  $H_0$  to  $H'$  by the series of increments  $d_1 H, \dots d_r H, \dots d_n H$  is the continued product

$P_1 \dots P_r \dots P_n$ . But every  $P$  which belongs to an interval for which  $H$  differs much from  $H_0$  is for that reason very small. Also for each interval  $P$  is less than unity. Therefore if  $H'$  is much greater than  $H_0$ , the continued product  $P_1 \dots P_n$  is inappreciably small, and infinitely smaller than it would be if  $H$  were throughout the interval  $t'$  nearly equal to  $H_0$ . The existence of our directing condition caused  $H$  to diminish, and its continued existence prevents  $H$  from again increasing beyond a small amount. The process, aided as we have assumed by Maxwell's demons, is in a defined sense irreversible.

22. Let us next assume that no external interference takes place; but the system, once started, is left undisturbed to its own mutual actions. What, under these circumstances, becomes of the chance we considered in Art. 21? It there appeared as the continued product of a number of factors, many of which were very small. It is now the single chance of the system having, when  $H = H_0$ , that particular set of coordinates and velocities of which the subsequent increase of  $H$  to  $H'$  is a necessary consequence. Let  $C_t$  denote this particular state. Then  $C_t$  is itself the necessary consequence of a certain initial state  $C$ . And therefore the chance that  $H$  shall ascend from  $H_0$  at time  $t$  to  $H'$  at time  $t + t'$  is the chance that the initial state, formed as we have formed it, shall be  $C$ . It may be that  $C$  is a very improbable initial state. If that can be proved, then the ascent of  $H$  from  $H_0$  to  $H'$  is improbable in the same degree. I am not aware that it ever has been proved. To say that  $C$  is improbable as an initial state because it leads to the subsequent increase of  $H$  would be *petitio principii*. If, however, it can be proved *aliunde* that  $C$  is improbable as an initial state, then we have a clearly defined sense in which one subsequent state is more or less probable than another, viz. as it is the necessary consequence of a more or less probable  $C$ . All successive states in the same course are equally probable.

23. There is indeed another sense in which, I think with less propriety, one state may be called more probable than another. We may prove namely that,  $P$  and  $P'$  being two possible states of the system, the initial state, formed as we have formed it or in some equivalent way, is more likely to be  $P$  than to be  $P'$ . That seems to be the sense in which Boltzmann asserts that the system, as  $H$  diminishes, passes from a more to a less probable state.

It follows from Art. 15 that if any of the factors  $f'F' - f'F$  differ from zero, the state in which  $\frac{dH}{dt}$  is negative is more

probable in this sense than the reversed state in which  $\frac{dH}{dt}$  is positive. But when  $f'F' = fF$  in all cases, which we may call the normal state, then the direct and the reversed state are equally probable. If, therefore, the last external disturbance which has happened to the system be recent,  $\frac{dH}{dt}$  is probably

negative. The physical importance of this result seems to me to consist in the fact that to any system in nature external disturbances are always happening, and they come generally at haphazard without regard to the state in which the system finds itself for the time being. And therefore the last disturbance generally *is* recent. But a process of this kind is not an irreversible process.

24. I think the conclusion to be drawn is that the  $H$  theorem does not prove, and we have at present no proof, that in our test system of elastic spheres the diminution of  $H$  is irreversible in the same sense as loss of kinetic energy by friction.

Nevertheless, without being irreversible, the process has a certain physical significance. Let us draw the curve for which  $t$  is the abscissa and  $H$  the ordinate. When  $H$  is very small,  $F'f' = Ff$  nearly, in all cases;  $\frac{dH}{dt}$  therefore, and also  $\frac{d^2H}{dt^2}$ , is very small. Therefore the curvature is very small.

When  $H$  differs much from its minimum, the curvature is generally considerable. It follows that on average of infinite time,  $H$  will have nearly its minimum value. Deviations will occur, but there is no proof that with increasing time they become less frequent or less important. There is no ultimate state into which the system subsides by an irreversible process; but there is a state in which on average of infinite time it will be. And this we may call, as we have already called it, the *normal state*.

25. The question whether in an undisturbed system the condition of independence can exist may be expressed in the following form:—Let  $S$  be the principal function of the motion. Then if  $x_1, y_1, z_1, x_2, y_2, z_2$  be the coordinates of two spheres at time  $t$ , their momenta are  $\frac{dS}{dx_1}, \frac{dS}{dx_2}$  &c. If then the points  $x_1, y_1, z_1$  and  $x_2, y_2, z_2$  are very near each other, have  $\frac{dS}{dx_1}$  and  $\frac{dS}{dx_2}$  any tendency to be of the same sign? The condition of independence, if complete, asserts that they have

no such tendency. *A priori* and directly that problem would not be easy to attack. Indirectly and *a posteriori* it can be shown that this tendency does exist. It follows, namely, from the fact that our molecules, if elastic spheres have finite radius, if centres of repulsive force have finite sphere of action, that a certain stream motion (defined *post*) must exist beyond the accidental stream which in Maxwell's distribution would exist if the molecules were mere material points.

And this tendency becomes inappreciable only when the density becomes inappreciable. Further this property holds for an infinite system, that is if our space S (Art. 8) is infinite, but the density, or aggregate volume of all molecules in unit of volume, is finite.

26. I define *stream motion* at a point thus :—Let P be the point,  $r$  the distance of any other point from P. Let  $\psi$  be a function of  $r$  which is everywhere positive, finite, and continuous, is equal to unity when  $r < c$  (a very small quantity), is of negative degree when  $r > c$ , and such that

$$\int_0^\infty 4\pi r^2 \psi \, dr \text{ is finite.}$$

And  $\psi$  being so defined, then let

$$\begin{aligned}\xi \text{ at } P &= \sum u\psi / \sum \psi, \\ \eta \text{ at } P &= \sum v\psi / \sum \psi, \\ \zeta \text{ at } P &= \sum w\psi / \sum \psi,\end{aligned}$$

in which  $u, v, w$  are the component velocities of a sphere, and the summation includes all our spheres. And I now define  $\xi, \eta, \zeta$  to be the components of *stream motion* at P.

27. Now consider two cases : case (1) the spheres, each of finite mass, have infinitely small diameters, so that no collisions occur. This system will be in stationary motion, if Maxwell's law of distribution prevails. Other laws may be possible, but I assume Maxwell's to exist. On this assumption we calculate the values of  $\bar{\xi}^2, \bar{\eta}^2, \bar{\zeta}^2$ . Case (2) the spheres have finite diameter. It can be proved, as I have shown in Chapter V. of a work recently published on the Kinetic Theory of Gases, that in this case the motion is not stationary if  $\bar{\xi}^2$  &c. have the same values as before. To make it stationary  $\bar{\xi}^2$  &c. must have greater values than they have in Maxwell's distribution. This means, by the definition of  $\xi$  &c., that spheres near to each other have a tendency to move in the same direction. And this again requires that the law of distribution of velocities shall be  $e^{-hQ}$ , in which Q is not the sum of squares only, but

contains products of the velocities, namely

$$Q = \Sigma(u^2 + v^2 + w^2) + \Sigma\Sigma b(uu' + vv' + ww').$$

Here every  $b$  is negative, and is a function of  $r$  the distance between the two spheres whose velocities are  $u$  &c. and  $u'$  &c., which function is very small unless  $r$  be very small. This I claim to have proved in my Chapter V. The calculations are indeed laborious. I hope that some one, with or without reading my chapter, will show us a more excellent way.

28. To show how the finite diameters of the spheres modifies  $\bar{\xi}^2$  &c. let us suppose at a certain instant in a certain region  $\frac{d\xi}{dz}$  is positive, and take the plane of the paper for that of  $x, z$ . Under these circumstances a sphere of finite diameter having velocity from left to right is more likely to experience a collision on its lower side, where  $\xi$  is less, than on its upper, and is therefore on average deflected upwards. A sphere moving from right to left is on average deflected downwards. The effect in either case is to increase  $\frac{d\xi}{dz}$ . If our molecules instead of being elastic spheres were centres of repulsive force of finite radius of action, the sphere moving to the right would experience on average a greater pressure on its under side. A sphere moving to the left a greater pressure on its upper side. The effect on  $\frac{d\xi}{dz}$  is the same as before. It follows that in the system of finite spheres  $(\frac{d\xi}{dz})^2$ , and therefore also  $\bar{\xi}^2$ , has greater value than when the spheres are infinitely small.

29. It may be said that in criticising Boltzmann's process I have set up a process of my own, namely the increase of  $\bar{\xi}^2$  &c., and it may be asked what is the directing condition in this process, and is the process irreversible or not? The answer is as follows :

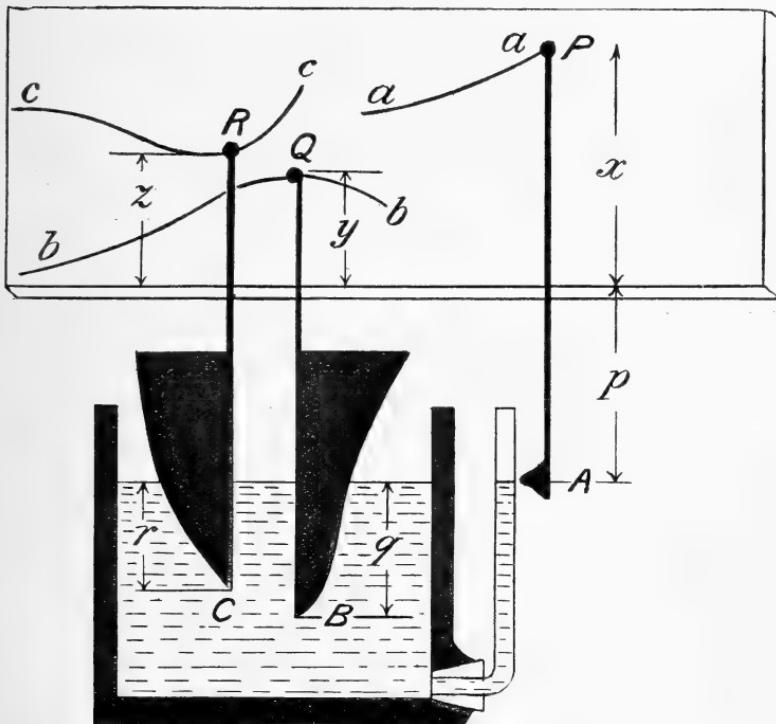
The finite dimensions of the molecules establish a limit beyond which the condition of independence cannot exist. Assuming that it can exist for molecules at considerable distance from each other, it cannot exist for molecules very near each other. The argument is that if we assume the independence absolutely, as I have done in my Chapter V., we obtain a result inconsistent with that absolute independence. For the form of distribution  $e^{-\lambda Q}$  is inconsistent with it. The assumption of absolute independence is then inadmissible.

*XLV. Petrovitch's Apparatus for integrating Differential Equations of the First Order. By W. A. PRICE\*.*

MICHEL PETROVITCH, Professor of Mathematics at Belgrade, has described in a recent number of the American Journal of Mathematics (vol. xxii. No. 1) an interesting instrument for integrating differential equations of the form  $Xdx + Ydy = 0$ .

Two curved templates, B, C (see fig. 1), made from thick plank are plunged into a rectangular tank of water. To B is attached a pointer Q, and to C a pointer R. A pencil P is

Fig. 1.



attached by a vertical rod to an index A, which is placed at the surface of the water.  $AP$ ,  $BQ$ ,  $CR$  can be moved vertically but not horizontally. The lengths  $AP$ ,  $BQ$ ,  $CR$  are drawn for convenience of the same length,  $l$ , though this is not essential. A board is moved horizontally behind PQR, and the templates B, C are moved in and out of the water by keeping Q, R upon curves previously drawn on the board.

\* Communicated by the Author.

The index A is continuously adjusted so as to be always at the water surface. The pencil P describes a new curve on the board. The ordinates of P, Q, R measured from a horizontal axis drawn on the board are  $x, y, z$  respectively. The meanings of the quantities  $p, q, r$  are seen from the figure.

If the sectional area at the water level of the B template be  $\phi(q)$ , and of the C template  $\psi(r)$ , and if the sectional area of the tank is M, we have for any small displacements of the templates

$$\phi(q)dq + \psi(r)dr + Mdp = 0.$$

Since

$$p = l - x,$$

$$q = x - y,$$

$$r = x - z,$$

the differential equation becomes

$$\phi(x-y) d(x-y) + \psi(x-z) d(x-z) = Mdx.$$

If  $t$  be the horizontal distance of the board from any fixed point the equations of the curves  $b$  and  $c$  may be written

$$y = f_1(t), \quad z = f_2(t);$$

and we have

$$[\phi\{x-f_1(t)\} + \psi\{x-f_2(t)\}]dx - [\phi\{x-f_1(t)\}f'_1(t) + \psi\{x-f_2(t)\}f'_2(t)]dt = Mdx.$$

a differential equation connecting the coordinates of P of which the curve  $aa$  is a particular solution. A series of such particular solutions is obtained by changing the quantity of water in the tank.

In the particular form in which the apparatus has been constructed by Prof. Petrovitch, the template C is fixed, so that  $f_2(t)$  is constant, and  $f'_2(t) = 0$ . The construction is seen in the figures 2 & 3. The paper is attached to a drum turned by an endless screw. The tank is narrow and the flat templates are placed one behind the other. The level of the water is observed by means of a vertical gauge-glass, on the opposite side of the large wooden block on the top of which the drum is mounted. The vertical rods are the guides for the moving templates, and for the rod which carries the pencil.

M. Petrovitch shows how the instrument may be used in a number of ways :

- (1) As an integrator.
- (2) As an integraph.

- (3) For the solution of equations of the form  $Xdx + Ydy = 0$ , or which may be reduced to that form.
- (4) To describe curves of the form  $\phi\{f(x)\}$  where  $\phi$  and  $f$  are known functions.

Fig. 2.

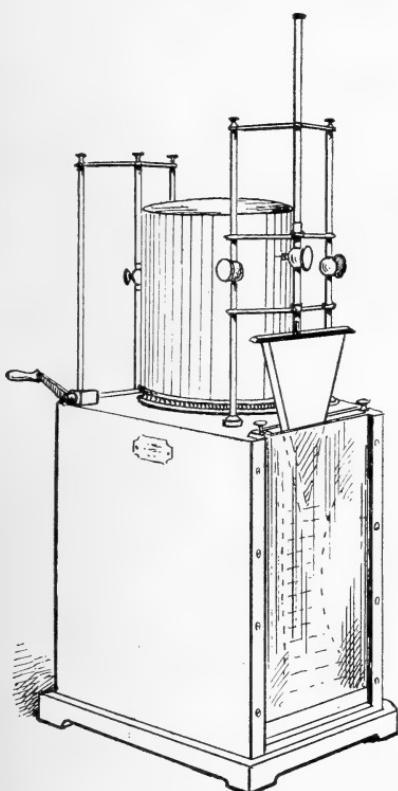
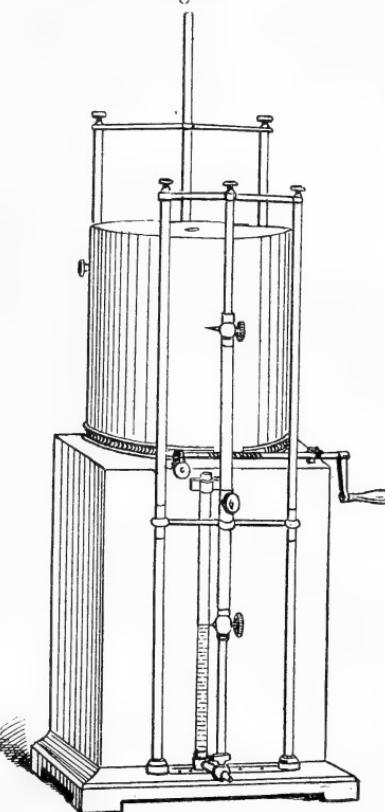


Fig. 3.



As examples of the possible uses of the instrument the following may be given :—

(1) The templates B, C (fig. 1) are triangular, having angles at B, C respectively, so that  $\phi(q) = mq$ ,  $\psi(r) = nr$ . The curves  $bb$ ,  $cc$  are straight lines, so that  $f_1(t) = bt$ ,  $f_2(t) = ct$ .

The differential equation becomes

$$(m+n) xdx - (mb+nc)(xdt+tdx) + (mb^2+nc^2)tdt = Mdx.$$

P describes a series of similar and coaxial ellipses.

In the particular case when the triangular templates are

similar, and the lines  $bb$ ,  $cc$  make angles of  $45^\circ$  with the vertical, P describes a series of concentric circles.

(2) Similar to (1) except that the template C is inverted, and the lines  $bb$ ,  $cc$  slope in opposite directions.

$$\text{Now } \phi(q) = mq, \quad \psi(r) = k - nr, \quad f_1(t) = bt, \quad f_2(t) = -ct.$$

The differential equation becomes

$$(m-n)x\,dx - (mb+nc)(x\,dt + t\,dx) + (mb^2 - nc^2)t\,dt + (k-M)\,dx = 0.$$

P describes a series of similar and coaxial hyperbolas.

(3) An harmonic synthesizer or tide predictor may be constructed of a number of rectangular or cylindrical plungers of sectional areas corresponding to the amplitudes of the several components, lifted and lowered in the tank by eccentrics of the proper periods. The level of the water will give the synthesis required.

(4) Suppose that in Petrovitch's instrument the curve described by the pointer attached to the moving template is a straight line  $y=t$ , and that the curve drawn by the pencil which follows the water-level is the curve  $x=\phi(t)$ , so that  $x=\phi(y)$ . Now cause the pointer to follow the curve

$$y = \frac{1}{n} \sin^{-1} t, \text{ so that the new curve drawn by the pencil is}$$

$$x = \phi\left(\frac{1}{n} \sin^{-1} t\right).$$

The area of the last curve is

$$\int \phi\left(\frac{1}{n} \sin^{-1} t\right) dt = \int \phi(\theta) \cos n\theta d\theta,$$

where  $t = \sin n\theta$ . Thus the Fourier components of the curve  $x=\phi(t)$  can be obtained if the form of the templates can be discovered which will develop the curve itself from a straight-line course for the pointer.

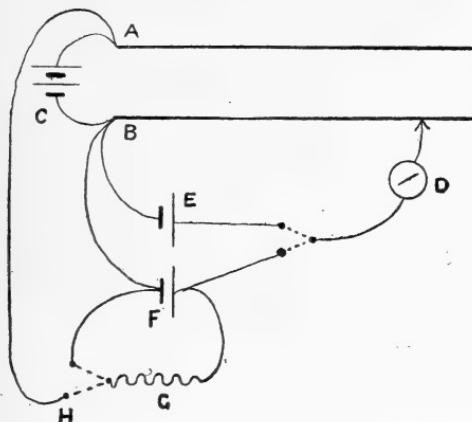
A great number of forms in which instruments can be made on the same general principle will readily suggest themselves. One consists of several vessels of different shapes containing water which may be transferred between the vessels by means of taps, or by a ladle. If the heights of the water-levels in the several vessels are  $x, y, z, \dots$  and the areas of the water-surfaces  $X, Y, Z, \dots$ ; then  $X\,dx + Y\,dy + Z\,dz + \dots = 0$  and curves or surfaces drawn by plotting the values of  $x, y, z$ , or by a mechanism attached to floats give solutions of the equation.

*XLVI. The Reversibility of Voltaic Cells.*  
By T. SIDNEY MOORE\*.

THE experiments described in this paper were carried out in order to test the reversibility of certain voltaic cells. Five cells have been treated:—Copper-zinc in sulphates, copper-cadmium in sulphates, copper-zinc in chlorides, and copper-cadmium in chlorides, in addition to the Clark cell. Preliminary experiments were carried out with nitrate cells, but the surfaces of the electrodes were spoiled by the nitrate solutions, and these cells have been put aside.

The diagram of the apparatus is shown in fig. 1.

Fig. 1.



ABCDEF shows the ordinary potentiometer arrangement, F being the experimental cell and E the Clark standard. G is an adjustable resistance, and by means of its three-way key H either the cell F may be placed in closed circuit with G, or the accumulators may be opposed to the experimental cell through the resistance G.

By means of this arrangement it is easy to get two determinations of the internal resistance of the cell F. Firstly, by means of the direct current when the cell F is in circuit with G, and, secondly, by means of the reading of the potentiometer when a current is running through F and in opposition to it. But to calculate the internal resistance from the latter experiment it is necessary to assume that the experimental cell is reversible. Thus, if we assume that the cell is reversible, the

\* Communicated by the Physical Society: read March 2nd, 1900.

difference between the values obtained for the internal resistance will measure the divergence of the cell from reversibility.

The results were calculated from formulæ which are easily deduced.

Let  $D =$  E.M.F. of experimental cell on open circuit.

$D_1 =$  " " " when running through resistance  $R$  ohms.

$D_2 =$  " " " when reversed through  $R$  ohms.

$B =$  " " the accumulators.

Current from cell through  $R = \frac{D}{R+r}$ , where  $r$  is internal resistance of cell.

$$\therefore \text{E.M.F. between poles of cell} = \frac{D}{R+r} \times R = D_1;$$

$$\therefore r = \frac{D - D_1}{D_1} \times R. \quad \dots \dots \dots \quad (a)$$

Or, if we regard the internal resistance as known, we have

$$D_1 = \frac{RD}{R+r}. \quad \dots \dots \dots \quad (b)$$

Now the reverse current through cell and resistance  $R$  ohms

$$= \frac{B - D}{R + r}, \text{ if the cell is reversible;}$$

$$\therefore \text{External E.M.F.} = R \times \frac{B - D}{R + r};$$

$$\therefore \text{E.M.F. between poles} = B - \frac{R(B - D)}{R + r} = D_2;$$

$$\therefore r = \frac{D_2 - D}{B - D_2} R. \quad \dots \dots \dots \quad (c)$$

Or, if we regard the internal resistance as known,

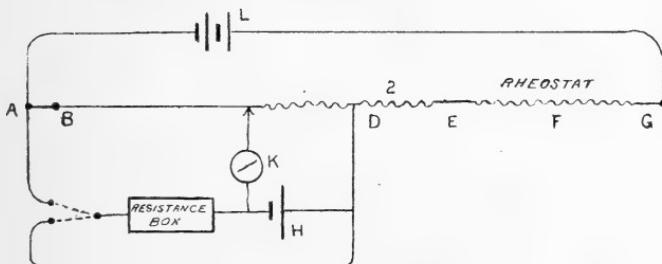
$$D_2 = \frac{rB + RD}{r + R}. \quad \dots \dots \dots \quad (d)$$

For the experiments a Crompton potentiometer was used, the arrangement of which is shown in fig. 2, together with the arrangement of the experimental cell and the resistance-box.

The accumulators L are connected with the circuit ABDEFG, and by means of the rheostat F and by balancing a Clark

cell against the accumulators it is easy to so adjust the current that 1 millimetre of the bridge-wire shall correspond to a change in E.M.F. of 1 millivolt. The bridge-wire is 1 metre long, and thus corresponds to 1 volt. Also the coils (1) and

Fig. 2.



(2) (see figure) are each of the same resistance as the bridge-wire, and thus each of these corresponds to 1 volt. So that it is very easy to get readings of any E.M.F. up to 3 volts.

The scale-wire extends to B, and the wire AB had a resistance equal to that of 43·4 millimetres of the scale-wire. Thus if the reverse current was taken between A and D, its E.M.F. was 2·0434 volts. If, however, as was sometimes the case, the coil (1) was taken out of the circuit, B was equal to 1·0434 volts.

The cell consisted of two glass vessels (short boiling-tubes) which had side-tubes blown in them. These side-tubes were connected by a short piece of indiarubber tube, to which was attached a screw-clip. It was found that, unless wads of cotton-wool were placed in the connecting-tubes, it was necessary to have solutions whose densities only differed in the fourth place. With the wads there is practically no diffusion, and the internal resistance is not unduly high. The solutions were made up approximately to the formula  $R \cdot 100 H_2O$ , where R is the molecular formula of any salt. The densities were then adjusted until they were approximately equal.

Solution.	Density at 13°.5 C.	Solution.	Density.	Temp.
Copper sulphate ...	1·081	Copper chloride ...	1·074	25°
Cadmium „ ...	1·082	Cadmium „ ...	1·079	16
Zinc „ ...	1·082	Zinc „ ...	1·076	25

*Results:*—(1) Cu, CuSO<sub>4</sub>, ZnSO<sub>4</sub>, Zn. (Daniell's cell.)

R.	r (direct ex-periment).	r (reverse exper-iment).	D <sub>1</sub> (observed).	D <sub>1</sub> (calculated).	D (observed).	D <sub>2</sub> (calculated).
4000 ...	ohms. 1389	ohms. 1392	volt. 0·8135	volt. 0·8135	volt. 1·3405	volt. 1·3397
6000 ...	1401·2	1389	0·8885	0·8895	1·2740	1·2736
12000 ...	1380·0	1378	0·9819	0·9835	1·1935	1·1937

For this cell D = 1·096 volt, B = 2·0434 volts.

The second column of the above was calculated from the observations by means of formula (a), the third column by (c), the fourth by (b), and the sixth by (d). The value of r used in the formulæ (b) and (d) was 1388·2, the mean of the six values obtained above.

In this experiment (and in all following) the copper electrode was electroplated and the zinc electrode cleaned with emery-paper and dilute sulphuric acid.

(2) Cu, CuSO<sub>4</sub>, CdSO<sub>4</sub>, Cd.

R.	r (direct exper-imen <sup>c</sup> ).	r (reverse exper-iment).	D <sub>1</sub> (observed).	D <sub>1</sub> (calculated).	D <sub>2</sub> (observed).	D <sub>2</sub> (calculated).
4000 ...	ohms. 1149·6	ohms. 1150·6	volt. 0·5740	volt. 0·5746	volt. ·8070	volt. ·8068
6000 ...	1128·6	1151·1	0·6220	0·6206	·7880	·7878
12000 ...	1118·4	1168·0	0·6760	0·6746	·7660	·7654

For this cell D = 0·739 volt at 14° C., B = 1·0434.

Mean value for r = 1144·4.

The cadmium used was a rod prepared by Johnson and Matthey, and was warranted to be over 99 per cent. cadmium. It was cleaned before each experiment by emery-cloth and dilute sulphuric acid.

(3) Cu, CuCl<sub>2</sub>, ZnCl<sub>2</sub>, Zn.

R.	r (direct experiment).	r (reverse experiment).	D <sub>1</sub> (observed).	D <sub>1</sub> (calculated).	D <sub>2</sub> (observed).	D <sub>2</sub> (calculated).
4000 ...	ohms. 304·9	ohms. 301·4	volt. 0·997	volt. 0·9997	volt. 1·141	volt. 1·1392
6000 ...	286·8	298·5	1·025	1·0230	1·119	1·1182
12000 ...	262·0	304·3	1·051	1·0474	1·097	1·0961

For this cell D=1·073 at 23° C., B=2·0434.

Mean value of r=293·1.

(4) Cu, CuCl<sub>2</sub>, CdCl<sub>2</sub>, Cd.

R.	r (direct experiment).	r (reverse experiment).	D <sub>1</sub> (observed).	D <sub>1</sub> (calculated).	D <sub>2</sub> (observed).	D <sub>2</sub> (calculated).
4000 ...	ohms. 479·9	ohms. 482·0	volt. 0·671	volt. 0·6704	volt. 0·782	volt. 0·7836
6000 ...	487·8	487·3	0·695	0·6956	0·7725	0·7738
12000 ...	493·1	490·4	0·722	0·7227	0·762	0·7633

For this cell D=0·752 at 16° 5 C., B=1·0434.

Mean value of r=486·75.

During the experiments, so long as diffusion was prevented, the E.M.F. of the cells remained constant. Even under the most unfavourable circumstances, viz. when the reverse current through 4000 ohms was running through the cell, the E.M.F. only altered about two millivolts. The conclusion to be drawn from the preceding results is that the cells treated, and consequently all similarly constituted cells, are reversible; for the differences in the values of the E.M.F.'s when calculated and when observed are not greater than might be expected as errors of experiment.

(5) A few experiments were also carried out with the Clark cell.

In the foregoing experiments the Clark standard consisted of two Clark cells in parallel. These were now separated, and one used as a standard and the other as the experimental cell. The internal resistance of this cell is, of

course, comparatively small, so that it was necessary to use smaller resistances for R than were used in the previous cases. R was therefore made equal to 3000, 2000, and 1000 ohms respectively.

R.	r (direct experiment).	r (reverse experiment).	D <sub>1</sub> (observed).	D <sub>1</sub> (calculated).	D <sub>2</sub> (observed).	D <sub>2</sub> (calculated).
3000 ...	ohms. 92·9	ohms. 98·8	volt. 1·389	volt. 1·3875	volt. 1·4515	volt. 1·4496
2000 ...	88·3	95·7	1·370	1·3667	1·4580	1·4585
1000 ...	.....	95·1	.....	.....	1·4825	1·4837

For this cell D=1·4315 at 16° C., B=2·0434.

Mean value for r=94·16.

With R=1000 ohms, it was found that the current was much too large, as the E.M.F. of the cell decreased very rapidly when running the current. But the reverse current gave a fairly good result, as might be expected. For the direct current would cause the solution of Hg<sub>2</sub>SO<sub>4</sub> to become weaker, and the solid present would not immediately saturate the solution. But the reverse current would cause Hg<sub>2</sub>SO<sub>4</sub> to be formed in the solution, which would therefore deposit some solid, but would at the same time remain saturated. Thus, all the results from the reverse experiments are better than the corresponding direct results; but considering the nature of the cell, these latter are fairly good.

Thus we may say that the Clark cell, besides the others treated here and those similar to them, is reversible.

These experiments were carried out at the suggestion and under the direction of Dr. Lehfeldt, of the East London Technical College, to whom I gladly acknowledge my debt.

Physical Laboratory,  
East London Technical College.  
October 1899.

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#### XLVII. *Notices respecting New Books.*

*Groupements Cristallins.* Par FRED. WALLERANT. Paris: Georges Carré & C. Naud, 1899. Pp. 1-81.

WHEN crystallization is allowed to take place in a solution which is not subject to any disturbance, we have the formation of well-defined and complete crystals. If, on the other hand, the liquid is violently stirred, we get, instead of large crystals, masses of small

crystals irregularly distributed. The relative positions of any two interpenetrating crystals may be very variable, but in some cases the grouping of the crystals is found to obey a definite law. It is this second class of crystal groupings that is studied by the author of the little book before us. After an introductory chapter on crystalline structure in general, and another which is devoted to a brief historical survey of the subject-matter in hand, the author considers the laws which govern the formation of regular crystal groupings. The remainder of the book is devoted to a classification and detailed examination, with illustrations, of the various forms of groupings, the last chapter dealing with the transformations which crystals may be made to undergo when subjected to mechanical stress. The book forms a valuable contribution to a difficult and intricate problem.

*Recherches Expérimentales sur les Oscillations Électriques.* Par A. TURPAIN. Paris : Librairie Scientifique A. Hermann. Pp. 1-154. 1899.

THE title of this book precisely describes its scope. It is an account of the author's important and careful researches on electro-magnetic waves ; many of the results contained in it have already appeared elsewhere, but all interested in the subject will be glad to have so complete and systematic an account of the author's work in book-form.

Perhaps the most striking feature of the book is the rigid, almost austere, exclusion of everything in the shape of mathematics. All controversial theoretical matter is carefully avoided, and the author abstains from the use of mathematical symbols in a way which cannot but be impressive to those who, to use the phrase of a well-known physicist, are accustomed to regard electrical phenomena through a cloud of analytical symbols.

The cautious accuracy of the author's exposition reminds one of the style of Faraday's *Experimental Researches*. The book is one which may be read with interest and profit by the beginner in the subject, and it will prove of still deeper interest to the advanced student.

In the first chapter, the author gives a detailed description of the vibrators and resonators used by him, and the methods of concentrating the Hertzian field between two wires or sheets of metal. Chapter II. deals with the methods of measurement. Chapter III. contains an experimental analysis of the field, the properties of the field concentrated by a couple of wires being deduced from those of a field concentrated by a single wire. Chapter IV. deals with the action of the resonator. In Chapter V. we have a most instructive account of the effects produced by using oil and water as dielectrics. Chapter VI. is a useful *résumé* of the principal experimental results established by the author ; and Chapter VII., which concludes the book, is devoted to a peculiar system of non-wireless Hertzian wave multiplex telegraphy devised by the author.

*Plane Trigonometry for Colleges and Secondary Schools.*  
By DANIEL A. MURRAY, Ph.D. (Longmans, 1899 : pp. xiii + 206.)

THE following extracts from the preface will serve instead of an analysis. "Careful consideration has been given both to the early difficulties and to the possible future needs of the beginner. An endeavour has been made to introduce the several topics in such a way that the pupil may have, from the very start, an intelligent idea of each step in advance, as well as of the ultimate purpose of the study." These statements have been verified and are true. The Author is evidently an excellent teacher of his subject. The text, figures, and typical examples (worked out) are all good. It is an elementary work which gives a clear account of Logarithms and provides a correct introduction to more advanced text-books. There is an Appendix which gives an "historical sketch" (such notes are also dispersed throughout the text), "projection definitions of the ratios," a note "on analytical Trigonometry," and one or two other advanced notes. There is a further collection of exercises for practice at the end of the book, with answers.

*Optical Activity and Chemical Composition.* By Dr. H. LANDOLT.  
Translated by J. McCRAE, Ph.D. Pp. xi + 158. London : Whittaker & Co., 1899.

THIS work is a translation of the eighth chapter of the first volume of Graham-Otto's *Lehrbuch der Chemie*. Considering the importance of optical tests in the examination of many organic compounds, it may be safely asserted that a book devoted to this subject fills a decided gap in chemical literature. Within the compass of some 150 small pages, Dr. Landolt gives a very complete account of the present state of our knowledge on this subject. The book is divided into three parts. Part I. deals with the general principles of optical activity. Part II. is concerned with the connexion between the rotatory power and the chemical composition of carbon compounds, and contains a very clear and interesting historical account of this matter. Part III. is devoted to the connexion between the degree of rotation and chemical constitution. In this concluding portion of the book the imperfect and fragmentary nature of our present knowledge regarding this subject is fully exhibited ; a vast amount of experimental work still remains to be done before any satisfactory general explanations can be arrived at.—The translation has been admirably executed by Dr. McCrae.

XLVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 416.]

January 24th, 1900.—W. Whitaker, B.A., F.R.S., President,  
in the Chair.

THE following communications were read:—

1. 'Fossils in the University Museum, Oxford: II.—On Two New Genera and Species of Crinoidea.' By W. J. Sollas, M.A., D.Sc., LL.D., F.R.S., V.P.G.S., Professor of Geology in the University of Oxford.

2. 'Fossils in the University Museum, Oxford: III.—A New Worm-track from the Slates of Bray Head, Ireland, with Observations on the Genus *Oldhamia*.' By W. J. Sollas, M.A., D.Sc., LL.D., F.R.S., V.P.G.S., Professor of Geology in the University of Oxford.

3. 'Contributions to the Geology of British East Africa: Part II.—The Geology of Mount Kenya.' By J. W. Gregory, D.Sc., F.G.S.

The three main zones of Kenya are characterized by different geological features. The long slope of the forest-belt consists in the main of volcanic ash, though the remains of secondary parasitic craters occur in it. The Alpine zone consists of coarser ash, agglomerates, and tuffs, interbedded with lava-flows and traversed by numerous dykes, with the remains of some secondary centres of eruption. The third zone, or central peak, consists of the plug which choked the central vent, of beds of agglomerate, and the thick proximal ends of the great lava-flows.

The rocks of the central core comprise an olivine-anorthoclase-nepheline-syenite with ægyrine, and a black glassy lava with numerous white phenocrysts of anorthoclase; this rock is allied in some respects to the pantellerites, but receives a special name both here and in its occurrence in lava-flows.

The dyke-rocks fall into two categories—a series of phonolites, and one of basalts and dolerites. One, at least, of the dykes is compound, including both these rock-types. The basic group ranges from basalts with little olivine to coarsely crystalline dolerite rich in that mineral.

The lavas belong to three main groups:—(1) Those of the nepheline-syenite series, (2) the phonolites, and (3) the basalts. The oldest lavas appear to be the phonolites, but they and the first group of lavas seem to have overlapped in age; the olivine-basalts, which reach the surface from a zone of secondary craters in the Alpine zone, are the latest in date. The first group of lavas are rhyolitic in aspect, and consist of a brown or green glass in which are embedded phenocrysts of anorthoclase, and green needles which show the optical characters of ægyrine. As these rocks do not conform to Rosenbusch's definition of pantellerites, a new name is proposed for them; the author considers that the pantellerites may be liparitic equivalents of the dacites, while these Kenya rocks correspond with the nepheline-syenites.

The structure of the phonolites is trachytic, the groundmass including abundant small, lath-shaped plagioclases; nepheline is not very abundant, and occurs in larger crystals than the other constituents, the chief of which is ægyrine. The basalts are often vesicular and columnar, and contain olivine, augite, magnetite, and apatite often in a glassy groundmass.

The pyroclastic rocks vary in texture from coarse to fine; they contain blocks of all types of the lavas, and also large crystals of anorthoclase.

The nepheline-syenite is the most deeply-seated, holocrystalline rock found on Kenya; and the mountain appears to represent a single, ancient, dissected, volcanic mass, with a shorter geological history and a narrower range of rock-types than its great companion volcano, Kilima Njaro. The author gives reasons for considering that all the different rock-types present may have resulted by differentiation from the olivine-anorthoclase-nepheline-syenite magma, although this involves the conclusion that in some cases the basic materials must have concentrated in the glass and solidified after the formation of the felspars.

4. 'Contributions to the Geology of British East Africa: Part III.—The Elæelite-Syenite and Fourchites intrusive in the Coast Series.' By J. W. Gregory, D.Sc., F.G.S.

The rocks described in this paper were given to the author by Mr. C. W. Hobley. Mount Zombo, situated in long.  $39^{\circ} 13'$  E. and lat.  $4^{\circ} 26'$  S., and 1519 feet high, is a massif of coarse-grained elæelite-syenite, consisting of anorthoclase, elæelite, usually allotriomorphic, and ægyrine. The rock must occur in the belt of Duruma Sandstone, unless the fossiliferous Jurassic shales run westward up the low valley of the Umba River. Associated with this massif is a series of dykes belonging to the olivine-less variety of monchiquites known as fourchites. Their phenocrysts consist of plagioclase, probably oligoclase, hornblende, and ægyrine, but augite and ilmenite are also present; the groundmass contains a certain amount of analcite.

Unfortunately there is some doubt as to the exact age of the Duruma Sandstone into which the fourchites are intrusive. The author gives an account of the different opinions as to the age of these rocks; the evidence at present available is only sufficient to prove that they are post-Carboniferous and pre-Callovian. The sedimentary series on the coast-lands of British East Africa and Usambara, in his opinion, may be provisionally arranged as follows:—

5. Pleistocene reefs, limestones, alluvium, and laterites.
4. Jurassic shales and sandstones; Kimeridgian, Oxfordian, and Callovian.
3. Possibly a pre-Jurassic part of the Duruma Sandstone.
2. Magarini sandstones; ?Triassic.
1. Sabaki shales: Upper Carboniferous.

It is, therefore, probable that the igneous rocks are not older than the early Mesozoic, and may be Jurassic or post-Jurassic.

February 7th.—W. Whitaker, B.A., F.R.S., President,  
in the Chair.

The following communications were read:—

1. ‘Foraminifera from an Upper Cambrian Horizon in the Malverns.’ By Frederick Chapman, Esq., A.L.S., F.R.M.S.

2. ‘Bala Lake and the River-System of North Wales.’ By Philip Lake, Esq., M.A., F.G.S.

In this paper the author begins by showing that topographically Bala Lake belongs to the same valley as the River Wnion—the valley of the Bala Fault; and he believes that the whole drainage of the valley originally flowed south-westward, and entered the sea near Barmouth.

He then examines the possible outlets, and shows that the lake is probably rock-bound in all directions except towards the south-west, where there is no conclusive evidence.

He describes the faults which occur near the watershed that separates the Wnion from the streams flowing into Bala Lake, pointing out that they are closely related to the form of the valley, and that the watershed coincides with a transverse line of fault. From this he infers that the formation of the lake is possibly due to earth-movements.

The watersheds of several other similar valleys are examined, and are shown to lie in one straight line; whence it is concluded that they must have been produced by some general cause, probably a slight differential movement.

The general drainage-system of North Wales is next discussed. Attention is drawn to the existence of a series of long and nearly parallel valleys running from north-east to south-west, which divide the region more or less completely into a number of strips. The drainage of each strip is now independent, and flows in most cases into the long valley lying south of it. But from the fact that the chief streams in each strip have their representatives (flowing in the same line) in the adjacent strips, it is concluded that before the formation of the long valleys the streams were continuous.

The centre from which these streams radiate lies in the high ground near the sources of the Conway; and the author believes that this was the centre of an original radial system of drainage, and that this radial system was subsequently broken up into sections, by the formation of the long valleys which now run from north-east to south-west—each of these long valleys carrying away the drainage of one of the sections. He attributes the formation of the long valleys to faulting.

February 21st.—W. Whitaker, B.A., F.R.S., President,  
in the Chair.

The following communications were read:—

1. ‘The Bunter Pebble-Beds of the Midlands and the Source of their Materials.’ By Prof. T. G. Bonney, D.Sc., LL.D., F.R.S., F.G.S.

The author states the results of occasional work in the Bunter

Conglomerate of Staffordshire. After a sketch of matter already published, he gives additional particulars of the lithology of the pebbles, more especially of the felstones and of some rather compact dark rocks. Of the former he has now obtained about thirty varieties: orthoclase-felsites and porphyrites, some with, others without quartz; several contain tourmaline, which sometimes has replaced biotite, sometimes felspar. One pebble exhibiting reddish spherulites in a dark matrix, once doubtless glassy, but now devitrified, is not like any British rock known to the author. Of the dark pebbles, some are fine-grained quartzites blackened with opacite; others, varieties of 'schorl-rock,' and two (which Dr. G. J. Hinde has kindly examined) are radiolarian cherts, which, however, cannot be more precisely identified.

The mode of transport and source of the pebbles are next considered. The reasons, already published, for a fluviaatile, as opposed to a marine, origin are briefly summarized. If the former be accepted, certain conditions must be satisfied, which bear directly on the position of the source. These beds represent the destruction of large masses of rock. If brought by rivers, those must have been important and powerful, of a continental rather than an insular type. Hence the necessary physical conditions exclude limited districts near the Midlands, such as the Wrekin, Lickey, Hartshill, and Charnwood, even if they included (which is not the case) the right types of rock. As regards the Longmynd, their argillites, if they occur, are not common; their conglomerates do not exactly resemble the Bunter pebble-beds; their 'Torridonian' is a quartz-rhyolite rather than a quartz-felspar grit. The rocks required cannot be supplied from either Wales, the Lake District, or the Pennine Range, and we have no reason to suppose them concealed under Eastern and South-eastern England. We have therefore to choose between a southern and a northern source. Cornwall and Devon might perhaps furnish the schorl-rocks; possibly also one or two varieties of felstone (though this is doubtful) and the right quartzites and quartz-felspar grits occur in the Budleigh Salterton pebble-bed. But the characteristic flat ellipsoidal pebbles of grit, dominant here, are not found in the Midlands. Physical conditions also seem opposed to a northward flow of the rivers of Britain in the earlier part of the Trias. In Scotland, however, we find the right varieties of quartzite, the Torridonian grit, and many felstones, some apparently identical with, others closely related to, those in the Midlands. The rarity of tourmaline-rocks in that region is the only difficulty in looking to it or its vicinity for the main source of these pebbles.

2. 'Further Evidence of the Skeleton of *Eurycarpus Owenii*' By Prof. H. G. Seeley, F.R.S., F.L.S., V.P.G.S.

XLIX. *Intelligence and Miscellaneous Articles.*

THE ECHELON SPECTROSCOPE.

Blythswood Laboratory, Renfrew,  
April 9th, 1900.*To the Editors of the Philosophical Magazine.*

GENTLEMEN,

THERE are one or two corrections which should be noticed in the paper on the Echelon Spectroscope, published in your last issue, by Lord Blythswood and myself.

On p. 395 the double-order photograph of the blue (4358) mercury line, with a field of 24,000 units, appears to exhibit considerable asymmetry; this, however, is in part due to an error of the nature described on p. 392, but chiefly to the fact that, for purposes of reproduction, the outer lines were artificially strengthened, and this has not been done with sufficient care. In no case was any measurable asymmetry observed in the dispersion of the outer components of the resolved lines.

Dr. Larmor has kindly pointed out a slip on p. 400 in the value of  $\frac{\delta\lambda_1}{\lambda^2 H}$ , which should be  $2 \cdot 2$  q. p. instead of  $2 \cdot 3 \times 10^{-13}$ ; on p. 402 the equation for the difference in frequency of the lines should be  $n_1 - n_2 = \frac{eHv^2}{2\pi m}$ .

Yours very truly,  
E. W. MARCHANT.

P.S.—The details of the photographs on p. 399 of the green mercury line, taken with strong magnetic fields, have disappeared in the reproduction.

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## ON AN INTERFERENCE METHOD OF MEASURING THE DIAMETERS OF DISTANT PLANETS AND STARS. BY M. MAURICE HAMY.

In 1868, Fizeau pointed out that the observation of interference-fringes might possibly furnish a method of finding an upper limit to the apparent diameters of stars.

If a screen with two parallel slits is placed in front of the object-glass of a telescope, and the latter is then directed towards a celestial object, a system of interference-fringes is, as is known, obtained in the focal plane. The fringes do not appear unless the apparent angle of the source situated in front of the apertures is sufficiently small. In fact, each point of the source produces its own system of fringes, and in order to avoid complete confusion of the fringes, it is necessary that the apparent angle  $\epsilon$  of the source, viewed from the first nodal point of the object-glass, should be less than the apparent angle of a fringe, viewed from the posterior nodal point.

This forms the basis for establishing an approximate relation between the diameter  $\epsilon$  and the distance apart of the slits which causes the fringes to vanish.

The method has been experimentally tested by Stephan (1873), who made use of the large telescope of the Marseille Observatory. On placing in front of the object-glass a lunular screen, which allowed the light to pass through the two opposite borders, he was enabled to infer the existence of an apparent diameter of  $0''\cdot2$ . In fact, the stars of the 1st, 2nd, and 3rd magnitudes observed have an apparent diameter inferior to this limit.

Since then, M. Michelson (about 1892) has made a careful study of the theory of these experiments, and has verified all its consequences, by first using terrestrial sources of various dimensions. Further, using a 12-inch equatorial, he has measured the diameters of Jupiter's satellites.

M. Maurice Hamy has taken up the study of this subject, with a view to substituting large slits, which allow a great deal of light to pass through, for the very narrow apertures employed in the previous researches. He has arrived at a formula which solves the problem. Experiments have been carried out with the large equatorial of the Paris Observatory. The first measurements were made under unfavourable atmospheric conditions (on June and July nights). Nevertheless, their results are very concordant. The differences from day to day are, in general, less than one-tenth of a second. On rejecting the highest numbers, which correspond to an increase in the apparent diameter due to irregular atmospheric refraction, the definite results for Jupiter's satellites are respectively

I.	II.	I.	IV.
$0''\cdot98$	$0''\cdot87$	$1''\cdot28$	$1''\cdot31$
Michelson's results are :—			
$1''\cdot02$	$0''\cdot94$	$1'\cdot37$	$1''\cdot31$

The agreement between the two sets of values is remarkable.

M. Maurice Hamy has applied the same method to the measurement of the apparent diameter of the planet Vesta, and finds for it  $0''\cdot54$ .

Now this is precisely the number found by Barnard by means of direct micrometric measurements made with the enormous telescope of the Lick Observatory; the interference method furnishes the same result with much greater ease.

The author concludes by showing that, in spite of its great sensitiveness, the interference method is powerless so far as the determination of the apparent diameters of stars is concerned. If, in fact, the sun were transported to a distance equal to that of the star  $\alpha$  Centauri, its apparent diameter would fall below the one-hundredth of a second; and in order to determine this, even with the interference method, the telescope would have to be more than 12 metres in diameter!

One may, it is true, imagine an interference apparatus which is applicable, theoretically, to the study of the diameters of stars and which does not require a telescope of extraordinary dimensions; but the experimental difficulties connected with it are so great that they do not appear to be capable of being surmounted.—*Séances de la Société Française de Physique*, Feb. 16th, 1900.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

JUNE 1900.

L. *On the Variation of the Electric Intensity and Conductivity along the Electric Discharge in Rarefied Gases.*  
By HAROLD A. WILSON, B.A., B.Sc., Trinity College, Cambridge\*.

1. *The Electric Intensity.*

GRAHAM † has given a number of curves showing very completely the variation of the electric intensity along several continuous discharges in rarefied nitrogen. In the following paper several similar curves are given obtained under somewhat different conditions, and with other gases as well as nitrogen. The results of some measurements of the conductivity of the discharge, between small platinum electrodes, along the whole length of the discharge are also given.

Skinner ‡ has shown that very near the anode the electric intensity is very small or zero when the positive column is not striated. He also mentions that with a striated positive column the potential-difference between the anode and an exploring-wire near it was a minimum when the exploring-wire was at a short distance from the anode, so that the apparent electric intensity near the anode was negative. These results are entirely confirmed by the observations described below.

\* Communicated by Prof. J. J. Thomson, F.R.S.

† W. P. Graham, Wied. Ann. lxiv. p. 69 (1898).

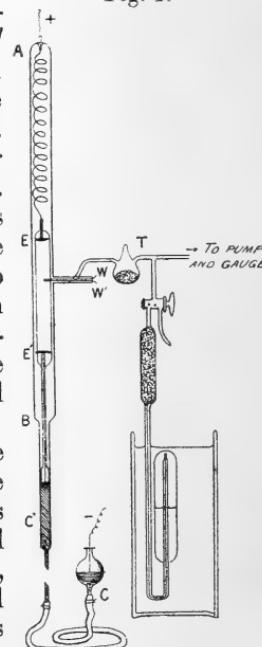
‡ Inaugural Dissertation, Berlin, 1899. "Ueber das Anodengefälle bei der Glimmentladung," C. A. Skinner.

The interest attaching to observations of this kind has been considerably increased since Prof. J. J. Thomson \* has shown how from the curves for the electric intensity to determine where the ionization and recombination principally take place, so that it was thought worth while to make a series of observations with the object of confirming and extending Graham's results.

The method employed was to measure the difference of potential between two exploring-wires, kept at a fixed distance apart in the discharge, which could be brought into any desired portion of the discharge by moving the electrodes between which the discharge took place.

The discharge-tube employed is shown in fig. 1. The glass tube A B in which the discharge took place between the electrodes E, E' was 50 cms. long and 2·5 cms. in diameter, and was supported vertically. The electrodes E, E' were thin disks of aluminium which fitted the bore of the tube loosely, and were made slightly convex towards each other. The electrodes were connected together by three parallel glass rods each 1 millim. in diameter, which passed through holes close to their circumferences. These glass rods were fused to glass tubes to which the electrodes were fixed, as shown in the diagrams. In this way the electrodes were kept at a constant distance apart, but were free to slide up and down in the tube A B.

Fig. 1.



The tube carrying the lower electrode E' was floated in mercury in the tube C, to which a barometer-column was attached by means of which the level of the mercury in C could be varied, and so the electrodes E, E' raised and lowered. The upper electrode E was connected by means of a spiral of fine brass wire to an electrode at A, and the lower electrode E' was connected with the mercury in C by a wire sealed through the lower end of the tube floating in the mercury.

The electrode A and the mercury in C were connected with the battery of 600 small secondary cells which was used to produce the discharge.

\* Phil. Mag. March 1899, p. 253.

At W a tube 1 cm. in diameter and 5 cms. long was joined on at right angles to the discharge-tube and two platinum wires W, W' were sealed in at the end of it. These wires extended to the centre of the discharge-tube, and were coated with glass except for 2 millims. at their extremities, which were one above the other and 1·5 millim. apart. The wires are shown on a larger scale in fig. 2. The difference of potential between W and W' was measured with a well insulated quadrant electrometer.

A telephone, galvanometer, and adjustable resistance were included in the discharge circuit, and during a series of observations the current through the tube was kept at a constant value.

The tube T was sealed on to a Töpler pump, McLeod gauge, and an arrangement for introducing any gas into the apparatus, &c.

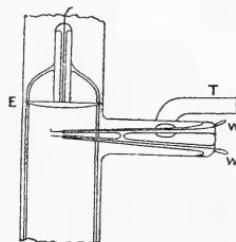
It was found that when a discharge was passing the wires W, W' took up their final potentials immediately, and that the electrometer-reading was not appreciably affected even by connecting either or both of them to earth through a very high resistance such as a piece of damp thread, which of course immediately discharged them when no discharge was passing. The insulation between the wires W, W' was very good, and they were able either separately or together to hold a static charge for a long time.

A millimetre-scale backed by a mirror was attached to the discharge-tube, and the position of the electrodes E, E' with reference to the wires W, W' read off on it.

The method of obtaining a series of observations was as follows:—The tube was first filled with the gas at the required pressure and the discharge started, if necessary, by means of an induction-coil. The current was then adjusted to the required value and its steadiness tested with the telephone. When a steady current of the required value had been obtained in a sufficiently pure gas at the required pressure the potential-difference between the wires W, W' was observed with the electrodes E, E' in a series of positions from that with the electrode E in contact with the wire W to that with the electrode E' in contact with the wire W'. The current was kept constant during the series of observations, and unless the gas pressure remained practically unchanged whilst the series was being taken the observations were rejected.

It was found very difficult to obtain entirely satisfactory

Fig. 2.

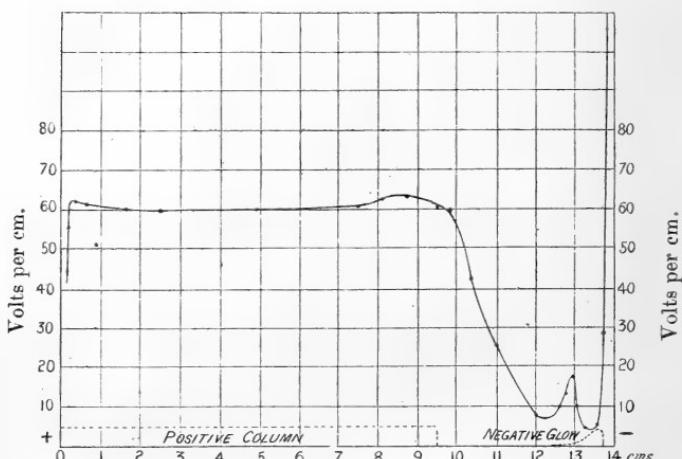


series of observations, partly owing to changes in the gas pressure which occur sometimes when the discharge is passed for any length of time, and partly owing to the difficulty of obtaining a sensibly steady discharge except within certain limits of current value.

Another source of trouble is the sputtering of the negative electrode which occurs even with aluminium electrodes, and forms a conducting coating on the walls of the discharge-tube which may cause the character of the discharge to change as the electrodes are moved into a different portion of the tube. The only remedy for this is to open the tube and remove the deposit as soon as it begins to have an appreciable effect. The backs of the electrodes were covered with disks of mica to prevent sputtering there.

The gases tried were air, nitrogen, and hydrogen. All were dried with  $P_2O_5$ , and the nitrogen was prepared from  $NaNO_2$  and  $NH_4Cl$ , and passed through  $FeSO_4$  solution and  $H_2SO_4$ . The hydrogen was prepared by electrolysis of dilute  $H_2SO_4$  and passed through  $KMnO_4$  solution. Oxygen which was used in some later experiments was prepared by heating pure  $KMnO_4$ . The light from the discharge was in each case examined with a pocket-spectroscope, and when no impurity could be detected in this way the gas in the tube was considered sufficiently pure.

Fig. 3.—Discharge in Nitrogen.  
Pressure 1·06 mm. Current 0·676 milliampere.



Some of the results obtained are shown in figs. 3, 5, 6, 7, 8. The distribution of light along the discharge is roughly indicated by the dotted curves.

Fig. 3 is for the commonest type of discharge with a uniform positive column. At each end of the positive column the electric intensity rises slightly, and then falls to a small value. The rise before the fall at the positive end of the positive column is often very considerable. The following numbers are for a discharge in air at 0·5 mm. pressure with current 0·28 millampere.

Distance from Positive Electrode. cms.	Electric Intensity. volts per cm.
1·8 .....	21
1·7 .....	19
1·2 .....	23
0·6 .....	27
0·35 .....	32
0·24 .....	33
0·16 .....	21
0·08 .....	0

At pressures above 1 millim. the fall in the intensity near the positive electrode occurs so near to the positive electrode that it is difficult to observe; but I do not think there is any reason to doubt that it still exists.

The "positive drop" at the surface of the positive electrode measured by Skinner (*loc. cit.*) was always noticed in these experiments when one of the exploring-wires came into contact with the positive electrode. It appears, as Skinner showed, to occur excessively close to the surface of the electrode, near which the intensity is zero or even apparently negative.

That the electric intensity near the positive electrode can be really negative seems unlikely, and it is consequently probable that the exploring-wires, when near the positive electrode, either fail to take up the potential of the surrounding gas, or else that the wires so disturb the discharge that their presence converts the very small positive intensity into a negative intensity at the place where the wires are. To obtain information on this point some experiments were tried in which the exploring-wires in the apparatus were replaced by fine platinum tubes from which a stream of mercury could be allowed to flow, breaking up into fine drops travelling two or three millimetres horizontally. It was thought that the jet of mercury would act as a "mercury dropper," and so take up the real potential of the surrounding gas. The platinum tubing used was 0·5 millim. external

diameter and 0·25 millim. bore, and was covered with a very thin coating of glass.

The apparatus is shown in fig. 4. The two tubes W, W' were sealed to glass tubes provided with taps which communicated with small insulated mercury-reservoirs. The positive electrode M was formed of mercury which could be raised and lowered, and into which the mercury from the two jets fell. The negative electrode N was kept fixed. The two tubes were connected to the electrometer.

With this arrangement it was found that the electric intensity indicated was not affected by running the mercury provided the stream of mercury was strong enough to go for a short distance horizontally before breaking into drops. Of course if big drops of mercury formed on the ends of the jets, these caused an alteration of the electrometer-reading : but otherwise running the mercury had no effect either in the positive column or very near to the positive electrode, where the intensity was found as before to be very small, or even negative.

The apparently negative intensity near the positive electrode was found to be most marked at low pressures and with small currents. Increasing either the current or the pressure diminished the length of the region of apparently negative intensity.

Since it is probable that the mercury-jets really took up the actual potential in the gas, we must conclude either that the presence of the wires or jets disturbs the discharge to such an extent as to reverse the sign of the intensity near the positive electrode, or that the intensity there is really negative. Such a region of negative intensity in the gas indicates the existence of a source of E.M.F. acting in the gas throughout the region in question. Such a source of E.M.F. may be imagined to be provided by positive ions shot off from the positive electrode by the excessively sudden potential-fall which occurs at its surface. Since the rise of potential in the region of negative intensity is usually only 1 or 2 volts, it is conceivable that the positive drop of 25 volts may project the positive ions from the positive electrode with enough energy to carry them against a negative intensity for a short distance, or they may be supposed to get across the region by diffusing simply.

Fig. 4.

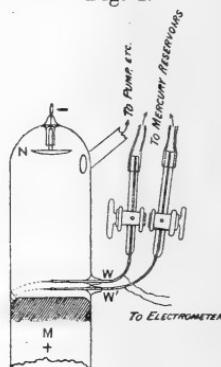
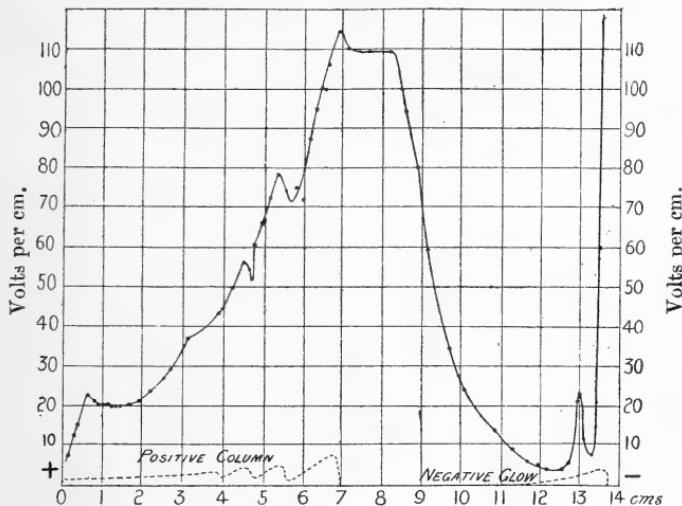


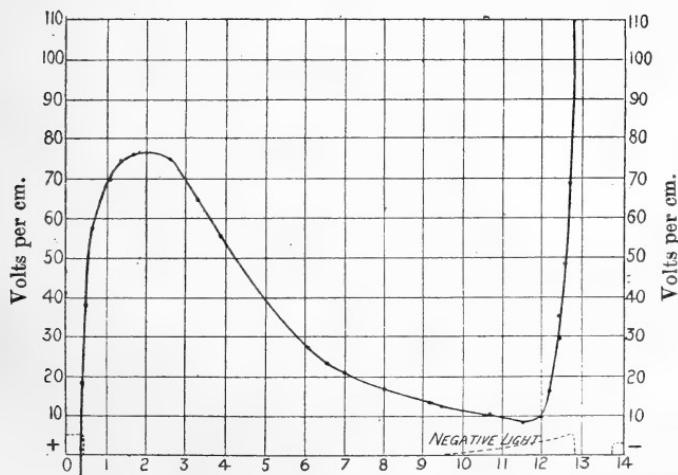
Fig. 5 is for a discharge with not enough E.M.F. to maintain a uniform positive column. A slight diminution of the current

Fig. 5.—Discharge in Nitrogen.  
Pressure 0·41 mm. Current 0·42 milliampere.



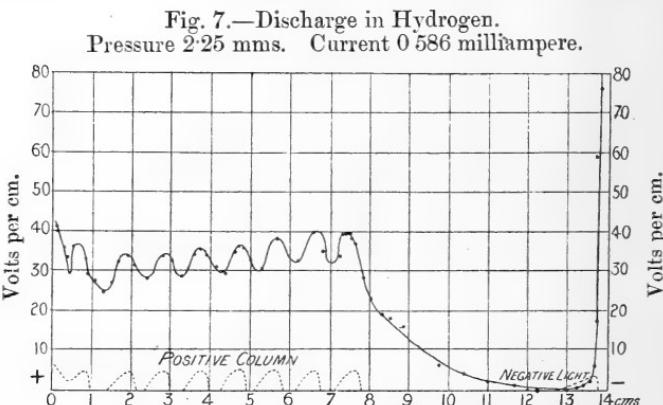
in the discharge shown in fig. 3 converted it into one like fig. 5. Thus the positive column appears to break down first at the positive end when the applied E.M.F. is diminished.

Fig. 6.—Discharge in Nitrogen.  
Pressure 0·117 mm. Current 0·19 milliampere.



In fig. 6 there is no positive column, and the low pressure enabled the fall near the positive electrode to be observed easily.

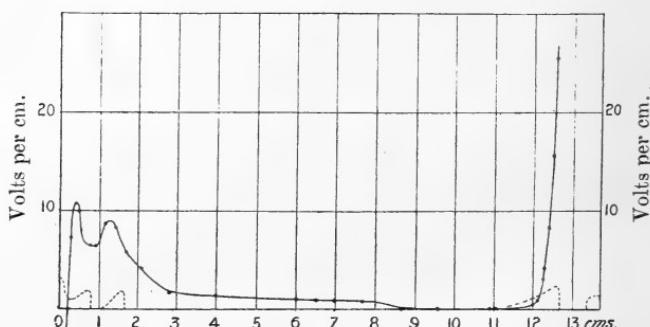
Fig. 7 shows the alternate rising and falling of the electric intensity in and between the striæ in the positive column.



The variations in the electric intensity near the positive electrode are very similar to those which occur between the positive column and the negative electrode, although crowded into a much smaller space. At each electrode there is a sudden drop of potential followed by a region of very small intensity.

Prof. Thomson has shown (*loc. cit.*) that where the ionization is in excess the intensity-curve must be concave upwards, and concave downwards where the recombination is in excess. From this we see that very close to the positive

Fig. 8.—Discharge in Air.  
Pressure 0·18 mm. Current 0·436 millampere.



electrode there is very intense ionization going on, and also in the negative glow and Faraday dark space ionization is in excess.

The form of the potential-fall curve in the electric discharge through a bunsen-flame is, as I have shown \*, very similar to that of the potential-fall curve in the discharge in rarefied gases, and in the flame nearly all the ionization appears to occur on the metallic electrodes when these are red hot. It seems to be the case in every kind of gaseous discharge that the ionization occurs most easily at the surface of a metal. In the ordinary discharge at low pressures it seems also very probable that all the ionization due simply to the electric intensity which may be called the primary ionization, occurs at the surfaces of the electrodes, for it is only close to the electrodes that the intensity is great enough to be supposed to produce ionization directly. The curves for the intensity given above do not show the sudden drops of potential and corresponding enormous intensities which occur at both electrodes, only the beginning of the rise of intensity near the negative electrode is shown. The negative ions formed at the surface of the cathode constitute the cathode rays, and produce the ionization which the intensity-curves show occurs in the negative glow.

The effect of this secondary ionization in the negative glow is to diminish the intensity there to a very small value. As the negative ions get separated from the positive ions they cause the intensity gradually to rise. This gradual rise in the intensity goes on until it is suddenly stopped by the appearance of the positive column. In the positive column more secondary ionization occurs. In the case of a uniform positive column the ionization at every point must be equal to the recombination. If it is supposed that the ionization in the positive column, like that in the negative glow, is due to the impacts of negative ions moving with great velocity, then it follows that the break in the gradual rise in the intensity which occurs at the end of the positive column is due to the intensity having become great enough to give the negative ions a velocity sufficient to enable them to produce as much ionization in the gas as the recombination which is going on. In the positive column the intensity, according to Hittorf, is independent of the current-strength, which shows that the amount of ionization going on there is proportional to the square of the current-strength. Thus if  $q$  is the amount of ionization going on in unit volume, assume  $q = a\iota^2$ , where  $\iota$  is the current-density and  $a$  a constant; also we have  $q = \alpha n_1 n_2$  and  $\iota = (k_1 n_1 + k_2 n_2) e X$ , using Prof. Thomson's notation (*loc.*

\* Phil. Trans. A. 1899.

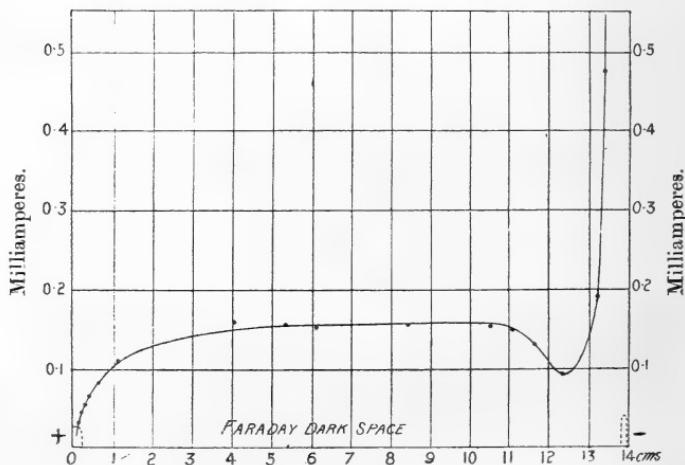
$$\frac{dX}{dx} = 0, \quad n_1 = n_2; \quad \text{so that } X = \frac{\sqrt{\frac{\alpha}{a}}}{e(k_1 + k_2)},$$

where  $X$  is the electric intensity, and  $\alpha$  is independent of  $t$ . Regarding the ionization as due to the impacts of the negative ions, we should have expected  $q$  to vary as  $n_2$ , and hence as  $t$ , not as  $t^2$ , in which case  $X$  and  $t$  would not have been independent.

## 2. The Electric Conductivity.

The discharge-tube already described was also used in the measurements made of the variation of the electric conductivity along the discharge. Small platinum plates each 1.5 mm. broad and 5 mms. long were welded to the wires  $W$  and  $W'$ , and the tube supporting these was cut off, turned through a right angle, and sealed on again so that the two small plates were fixed in the centre of the discharge-tube facing each other 1.5 mm. apart and with their long edges horizontal.

Fig. 9.—Discharge in Oxygen.  
Pressure 1.32 mm. Current 1.75 millampere.



The current between them produced by one Clark cell whilst the discharge was passing was measured. This current was found approximately proportional to the number of cells used up to ten cells in all parts of an ordinary discharge such as that shown in fig. 5. The current was measured first in

one direction and then in the other, and the mean of the two results, which never differed much, was taken. The Clark cell and galvanometer were well insulated, so that the small electrodes could take up the potential of the discharge. The platinum plates disturbed the luminous parts of the discharge to some extent. This was especially noticeable in a striated positive column unless the striae were widely separated so that their dimensions were large compared with the plates.

Some of the results obtained are shown in figs. 9, 10, and 11.

Fig. 9 is for an almost dark discharge with only thin layers of light at each electrode.

Fig. 10.—Discharge in Oxygen.  
Pressure 0·467 mm. Current 1·52 millampere.

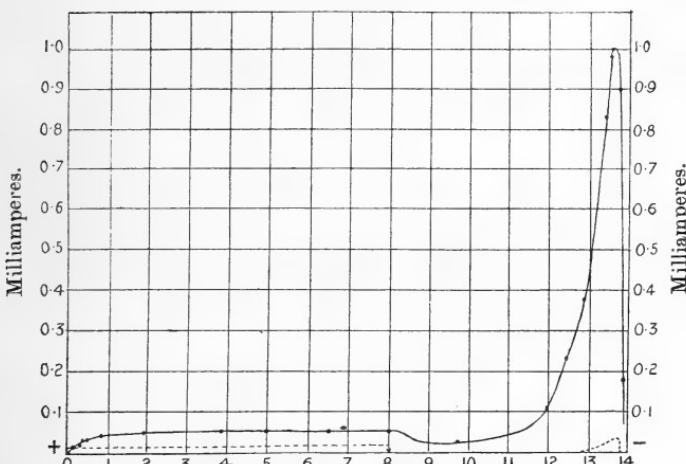
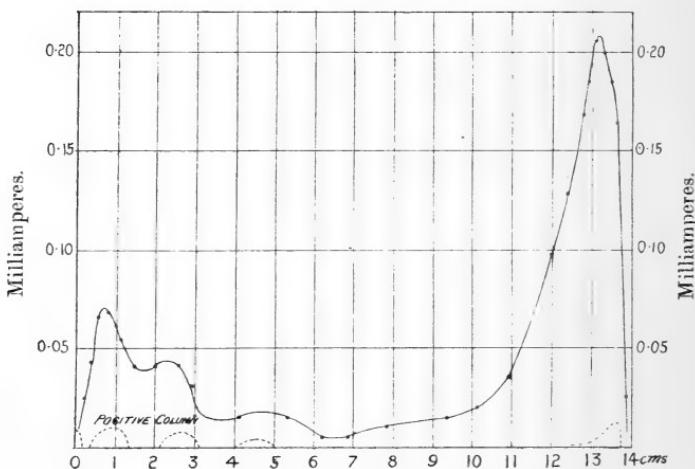


Fig. 10 is for an ordinary discharge with a uniform positive column. The current between the small electrodes does not vary as might have been expected from the known variation of the electric intensity along such a discharge. The most notable variation is in the Faraday dark space where the conductivity is less than in the positive column, whilst the electric intensity in the Faraday dark space is also much less than in the positive column. Near the negative glow the conductivity rises, as we should expect from the small intensity observed there, and falls again to a small value in the Crookes's dark space. The conductivity near the positive electrode is very small.

Fig. 11 shows the variations in the conductivity in a striated positive column.

Fig. 11.—Discharge in Air.  
Pressure 0.30 mm. Current 1.03 milliampere.



The conductivity falls between the striæ apparently instead of rising, as the intensity-curves lead one to expect. It is very probable that the radiation which the discharge emits may produce ionization on the small platinum electrodes, which would increase the apparent conductivity of those parts of the discharge which emit radiation. Thus the negative glow and the luminous parts of the positive column conduct better than the dark parts of the discharge.

The fall in the conductivity near the positive electrode probably corresponds to the increase in the intensity which usually occurs there before the drop to zero close to the electrode.

In conclusion, I wish to say that my best thanks are due to Prof. J. J. Thomson for valuable suggestions and advice during the carrying out of these experiments at the Cavendish Laboratory.

*L1. On the Distillation of Liquid Air, and the Composition of the Gaseous and Liquid Phases.—PART I. At Constant Pressure.* By E. C. C. BALY\*.

THE experiments described in this paper were commenced with a view of obtaining the relation between the temperature and the composition of the gas evolved from liquid air boiling under atmospheric pressure, so as to render possible the determination of the temperature of boiling air by the analysis of the gas evolved. They were, however, extended beyond this, and analyses were made of both the liquid and gaseous phases for all mixtures of oxygen and nitrogen, thus completing the investigation of the distillation of liquid air under constant (atmospheric) pressure.

The measurements of temperature were all made by means of a Callendar compensated hydrogen-thermometer. This instrument, which is a constant-pressure apparatus, differed from Callendar's description † in that the measurement of volume-change was read by admission of mercury into a graduated burette, instead of being weighed. The temperature as shown by Callendar may be calculated from the

$$\text{equation } T = \frac{V_0 T_2}{V_1 - V_2};$$

where  $V_0$  is the volume of the thermometer-bulb;

$V_1$  the total volume of the thermometer-bulb and the graduated burette;

$V_2$  the volume of gas measured in the burette during the experiment; and

$T_2$  the absolute (hydrogen) temperature of  $V_2$ .

In the thermometer used throughout the experiments, the volume  $V_0$  (at  $15^\circ$ ) was 28.655 c. c. and the total volume  $V_1$  was 129.590 c. c. The adjustment in order to make both sides of the apparatus, *i.e.* the compensating side and the thermometer side, quite equal in volume, was very carefully performed by means of the burette and then connexion was opened between the two sections so as to ensure there being an equal mass of gas on each side. The filling with hydrogen was very carefully carried out. The whole apparatus was thoroughly exhausted, and pure hydrogen was admitted to approximately 760 mm. pressure. The hydrogen was prepared from the palladium alloy, the first fractions which came off the palladium being rejected, and was dried over phosphorus pentoxide. Every care was taken in the filling,

\* Communicated by the Physical Society: read March 2, 1900.

† Proc. Roy. Soc. vol. 1, p. 247.

and the thermometer was several times refilled during the work.

The correction for the contraction of the glass bulb was also determined, and an attempt was made to measure the coefficient of expansion of glass between the limits  $-190^{\circ}\text{C}$ . and  $20^{\circ}\text{C}$ ., the usual limits of the experiments. The apparatus was a very simple one, as shown in fig. 1, and depended on the contraction of a glass tube of known length. A tube A was taken, which just slipped through the contracted neck of the tube B. Both tubes were sealed at their lower ends, and A rested on the bottom of B by a fine glass point, to minimise heat-conduction as far as possible. The whole apparatus was dipped into liquid air, while water was kept running through the inner tube A, thereby cooling B while A was kept warm. The contraction suffered by B was measured by observing with a micrometer the distance between two lines, etched one on A and the other on B, before and during the cooling. The apparatus worked very well, and a satisfactory measurement was obtained in which the total length of B cooled was 89.0 cm. The mean linear coefficient found was .0000073, Regnault's measurement between  $0^{\circ}$  and  $10^{\circ}$  being .0000085.

The measurements of temperature were corrected in accordance with the above found coefficient, the volume of the thermometer-bulb being taken as  $28.655(1 - .0000219t)$ .

For the temperatures dealt with in these experiments the correction was about  $0^{\circ}.37$ .

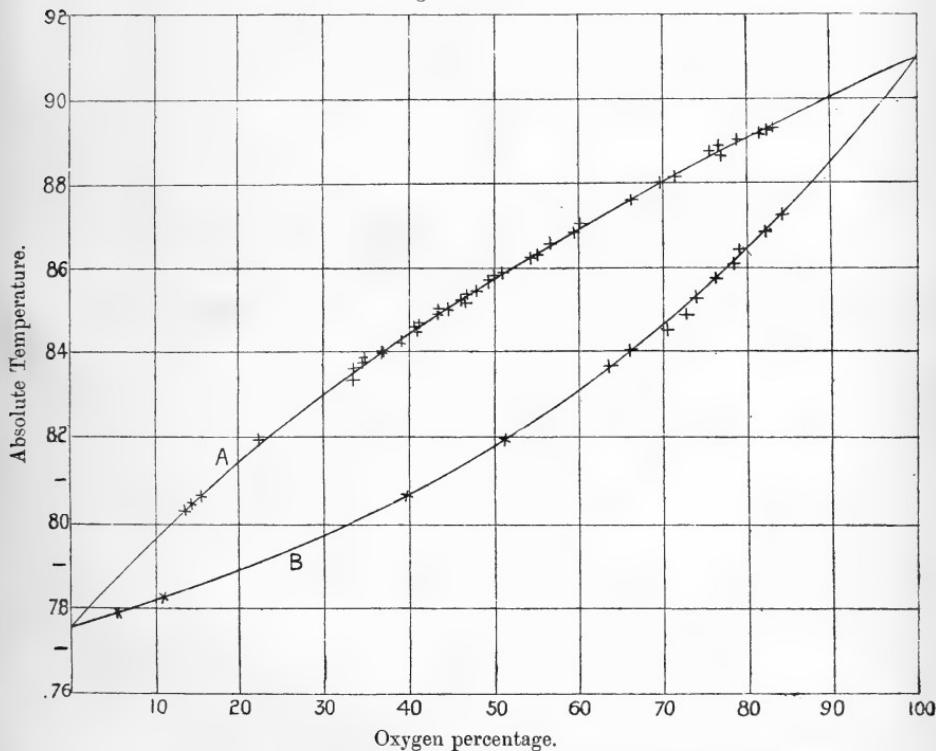
The probable accuracy of the results with the thermometer may be judged from the volume of the thermometer-bulb, 28.655 c. c., which caused the probable error to be very small. The reading of the volume of the gas in the burette was certainly accurate to .02 c. c., which means a maximum error of about  $0^{\circ}.02$ . In practice, however, the results agree better than this; for two determinations of the boiling-point of oxygen, and two of the boiling-point of nitrogen, differ respectively by only  $0^{\circ}.01$ , the measurements being made several days apart. The volumes of the various portions of the thermometer were most accurately determined, and there seems every reason to trust the measurements made with it. As regards the practical use of the instrument, too much cannot be said in praise of it. It is extremely quick to take up temperature-changes and very rapidly worked, and generally a most convenient and simple apparatus to use.

Fig. 1.



In the experiments on the composition of the vapour, the method of working was very simple. The thermometer-bulb was immersed in the liquid air contained in a vacuum-jacketed vessel, the top of which was loosely stoppered with cotton-wool. Samples of the gas evolved were taken from time to time as the air boiled away, by means of a tube passing through the cotton-wool, and the thermometer reading was noted at each time. The samples of gas were afterwards analysed by means of burning phosphorus, and the results plotted as percentages of oxygen, against the corresponding absolute temperatures. Several series were thus obtained, and the ends of the curve, that is to say where the mixture contained great excess of nitrogen or oxygen, were obtained by mixing liquid oxygen or nitrogen, as the case might be, with the liquid air. The curve drawn

Fig. 2.



through the points so obtained was completed by the determination of the boiling-points of nitrogen and oxygen, and it was found that the extrapolated curve met these points absolutely. The smoothed curve is shown on fig. 2 (curve A),

with most of the observed points marked with a cross, many of which are double. This curve has been plotted on a much larger scale, and as it is likely to prove of use in any work connected with liquid air, the following points read therefrom will serve for its reproduction :—

Temperature (absolute).	Percentage of Oxygen.	Temperature (absolute).	Percentage of Oxygen.
77.54	0.00 B.P. of Nitrogen.		
78.0	218	85.0	44.25
78.5	438	85.5	48.17
79.0	680	86.0	52.19
79.5	933	86.5	56.30
80.0	1200	87.0	60.53
80.5	1478	87.5	64.85
81.0	1766	88.0	69.58
81.5	2122	88.5	74.37
82.0	2360	89.0	79.45
82.5	2673	89.5	84.55
83.0	2995	90.0	89.80
83.5	3335	90.5	95.10
84.0	3686	90.96	100.00 B.P. of Oxygen.
84.5	4045		

If the above points be plotted and the curve drawn, the complete relation will be obtained, and the temperature of boiling air can be read direct therefrom if the composition of the gas evolved be found.

In order to further investigate the subject, a similar series of experiments was carried out in connexion with the composition of the liquid phase and its relation to the temperature. The samples were taken by means of a finely drawn piece of capillary tubing which dipped into the liquid. This was connected with a filter-pump which was kept running during the experiments. Samples of the gas were taken from a T-piece between the capillary and the filter-pump. The liquid air did not fractionate in the capillary, but boiled rapidly away as it rose in the tube out of the vacuum-jacket ; and samples were thus obtained of the mixture of oxygen and nitrogen which composed the liquid. Readings were taken as before on the thermometer, and the experiments were carried out, generally speaking, as in the case of the vapour phase above described. The results obtained were plotted, percentages of oxygen against temperature, and the curve thus obtained is shown on fig. 2 (curve B).

This curve has also been drawn on the large scale, and the following points read therefrom may be of interest :—

Temperature (absolute).	Percentage of Oxygen.	Temperature (absolute).	Percentage of Oxygen.
77·54	0·00	84·5	69·31
78·0	8·10	85·0	72·27
78·5	15·25	85·5	75·10
79·0	21·60	86·0	77·80
79·5	27·67	86·5	80·44
80·0	33·35	87·0	82·95
80·5	38·53	87·5	85·31
81·0	43·38	88·0	87·60
81·5	47·92	88·5	89·82
82·0	52·17	89·0	91·98
82·5	55·94	89·5	94·09
83·0	59·55	90·0	96·15
83·5	62·93	90·5	98·16
84·0	66·20	90·96	100·00

The two curves A and B represent the complete fractional distillation of any mixture of oxygen and nitrogen under 760 mm. pressure. For they show the boiling-point of every mixture of oxygen and nitrogen at 760 mm., and also the temperature at which any mixture of oxygen and nitrogen will liquefy and the composition of the liquid formed. It is evident that the lines of equal temperature cut the two curves at points of corresponding equilibria; that is to say, the compositions of liquid and vapour phases in equilibrium at each temperature. In connexion with these corresponding compositions of liquid and vapour, F. D. Brown \* suggested that in a distillation of a mixture of two liquids under constant pressure, the following formula might express the relation between them :—

$$r' = r \times \frac{P_1}{P_2},$$

where  $r'$  is the ratio of components in the vapour phase, and  $r$  the corresponding ratio in the liquid phase, and  $\frac{P_1}{P_2}$  the ratio of the vapour-pressure of the two components. This formula, however, assumes the validity of Raoult's law for every possible mixture. In an actual experiment, however, Brown found that it did not hold good, but that in the equation  $r' = r \times C$ ,  $C$  was remarkably constant.

\* Chemical Society's Transactions, xxxix. p. 304.

But this relation does not hold in the case of air, as the following results show :—

Temperature.	$\frac{r'}{r}$	Temperature.	$\frac{r'}{r}$
77.9	.2416	86.4	.3141
78.2	.2495	88.2	.3274
78.5	.2582	89.2	.3406
79.9	.2710	90.1	.3592
81.4	.2828	90.5	.3725
83.2	.2934	90.7	.3806

It will be seen that  $\frac{r'}{r}$ , instead of being constant, has a steadily increasing value with rise of temperature.

Lehfeldt, in his paper on "The Properties of a Mixture of Liquids"\*, showed that in Brown's case the logarithms of the ratios corresponding in the liquid and vapour phases had a linear relation; that is to say

$$\log r' = a + b \log r.$$

Inasmuch as this relation held so well for Brown's results, the logarithms of the corresponding ratios with air were plotted, and, as shown in fig. 3, a linear relation was found to exist in this case. The logarithms of 100  $r$  and 100  $r'$  were plotted for greater convenience. The points shown through which the curve is drawn were found for each half degree rise of temperature. The general accuracy of the results is shown by this curve, the departure of the points from the straight line being hardly appreciable. The large curves of percentages of oxygen against temperature were smoothed to a slight extent by reference to the logarithmic curve, though this made no change except to remove two slight irregularities which had not before been noticed.

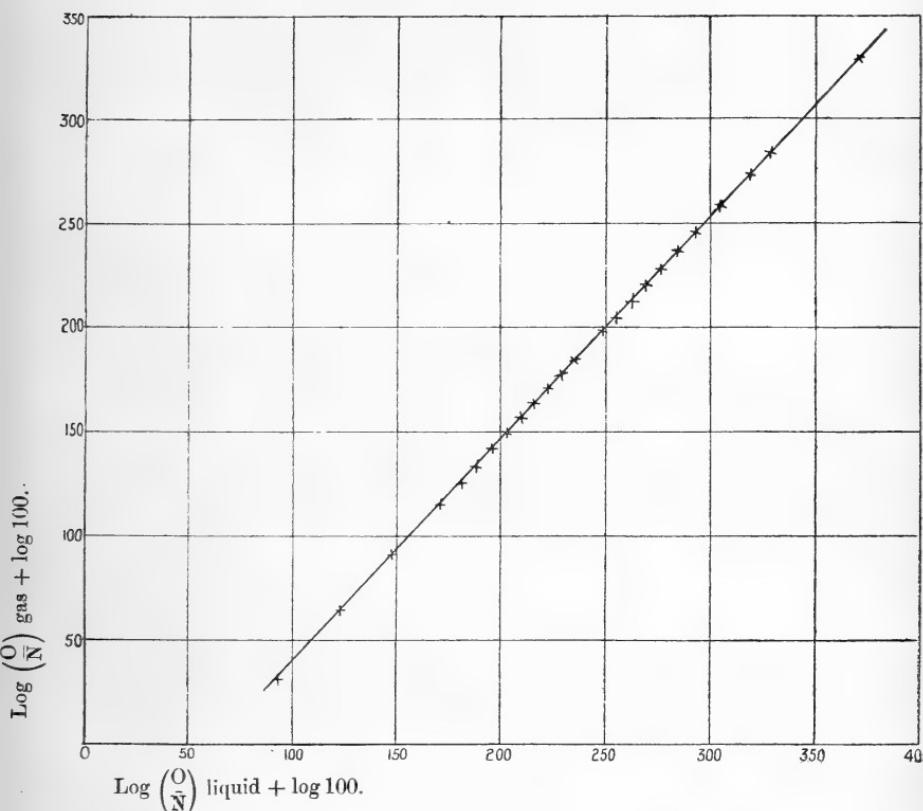
The values of the constants  $a$  and  $b$  in the equation  $\log r' = a + b \log r$  were first calculated from two pairs of readings from the smoothed logarithmic linear curve. As, however, these did not agree very well, 22 readings were made, and the most probable value calculated by the method of least squares, which gave the results

$$a = .2097.$$

$$b = 1.06737.$$

\* Phil. Mag. [5] xl. p. 397.

Fig. 3.—Relation between Logarithms of Ratios of Oxygen and Nitrogen in Gas and Liquid phases.



The most probable relation, therefore, between the corresponding ratios throughout the distillation is

$$r' = 2097 \times r^{1.06737},$$

where  $r' = 100 \times$  ratio in vapour,  
and  $r = 100 \times$  ratio in liquid.

The following series of calculated and observed ratios shows the accuracy of the above equation (see table on p. 524).

As regards the boiling-points of oxygen and nitrogen, the values given by previous experimenters differ to some extent from those given above, but they have not all been compared at the same pressure. Of the boiling-points of oxygen, the two latest are by Olszewski\*, in his comparison of hydrogen

\* 'Nature,' liv. p. 377.

Temperature.	Ratio in Vapour. Observed.	Ratio in Vapour. Calculated.
79	.073	.072
80	.136	.137
81	.215	.215
82	.309	.310
83	.428	.432
84	.584	.586
85	.794	.795
86	1.09	1.09
87	1.53	1.55
88	2.29	2.30
89	3.87	3.87
90	8.81	8.87

and helium thermometers, and by Estreicher\* on the saturation pressures of oxygen. Olszewski's measurements were five in number, and the means from the two thermometers were as follows :—

Pressure.	Temperature abs.
741 mm.	90°35
240 "	81°15
90·4 "	74·25
12·0 "	63·75
9·0 "	62·32

In order to complete the vapour-pressure curve for the above, the ratios of the temperatures giving equal vapour-pressure with water and oxygen were plotted against the water temperatures according to Ramsay and Young's equation †. The vapour-pressure of water were taken from Regnault's values as corrected by Broch. From the straight line passing through the points, data were calculated for the vapour-pressure curve. This was drawn, and gave the boiling-point at 760 mm. as 90°.60 absolute.

As regards Estreicher's measurements, of which there are 44, they have been plotted directly, but it is difficult to draw a curve through them for they are very scattered at the higher temperatures. The point he gives as the mean of 25 observations,  $P=743\cdot8$  mm.  $T=90^{\circ}44$ , agrees very well with Olszewski's values, and so do two more points. If, then, these points be taken as correct and the curve drawn, this can only be done by neglecting entirely many points at medium pressures. The curve, then, is almost superposed on

\* Phil. Mag. (5) xl. p. 454.

† Ibid. (5) xx. p. 515, xxi. pp. 33, 135.

Olszewski's. On the other hand, if the points at intermediate pressures be given some value, a very fair curve can be drawn which very nearly gives the same boiling-point as found on the Callendar thermometer as above, viz.  $90^{\circ}96$  abs., the actual point being  $90^{\circ}90$ . Which curve to adopt as best expressing his results I do not know, for no data are given of the 25 observations whose mean is given as one point. The difference between the boiling-point I have given and that found by Olszewski is  $0^{\circ}36$ .

Of the boiling-point of nitrogen, Olszewski\* gives a measurement in his series of five vapour-pressures, which are as follows :—

Pressure.	Temperature (abs.).
35 atmospheres	$127^{\circ}0$
31        "	$124^{\circ}8$
17        "	$116^{\circ}5$
1        "	$78^{\circ}6$
60 mm. (melting-point)	$59^{\circ}0$

The straight line of Ramsay and Young's ratios was drawn for these points. The last two by no means agree, and were therefore given equal weight. The vapour-pressure curve was drawn, and the boiling-point of nitrogen was given as  $77^{\circ}38$ . The difference, therefore, between the boiling-point I have given and that obtained by smoothing Olszewski's numbers is  $0^{\circ}16$ . Olszewski's values for the boiling-points for the two gases are thus both lower than the ones I have found.

In order to test Brown's suggestion that the ratio of the partial vapour-pressures of the two components in the liquid directly determines the composition of the vapour, it was necessary to make measurements of the vapour-pressures of oxygen and nitrogen with the temperatures referred to the Callendar thermometer. Since these vapour-pressures were only required between the temperatures  $77^{\circ}$  and  $91^{\circ}$  absolute, two points on each curve were sufficient, and the complete curve was drawn by the Ramsay and Young method. Of these two points, the pressure of 760 mm. at the boiling-point was one, and for the other it was necessary to determine the vapour-pressure of each gas at the boiling-point of the other. This was carried out first for nitrogen by immersing a small bulb containing atmospheric nitrogen into pure liquid oxygen, and then measuring the pressure under which it liquefied.

The mean of four readings was  $p=2805^{\circ}4$  mm.,  $T=90^{\circ}96$ .

\* *Compt. Rend.* xcix. p. 133.

This result very nearly lies on the curve of Olszewski's smoothed results.

The two points  $p=760$  mm.  $T=77^{\circ}54$  and  $p=2805$  mm.  $T=90^{\circ}96$  were plotted by Ramsay and Young's method, and the vapour-pressure curve drawn.

The vapour-pressures of chemical nitrogen were also determined. These were carried out similarly to those of atmospheric nitrogen with some intermediate points taken in liquid air. The boiling-point was not actually measured owing to the difficulty of preparing a sufficient quantity of liquid chemical nitrogen. The Ramsay and Young ratios were calculated and extrapolated to 760 mm., and from the straight line the vapour-pressures were obtained. The values obtained from the complete curve are given in the second column. Olszewski's values are continued up to  $124^{\circ}$  absolute.

The measurement of the vapour-pressure of oxygen was carried out very similarly to that of nitrogen. A large quantity of liquid nitrogen was made, and a small bulb connected with a store of pure oxygen from  $\text{KMnO}_4$  was surrounded with it. When the bulb was about a quarter full of liquid oxygen, it was connected with a gauge and the pressure read. Two series of measurements were made with one preparation of oxygen, and a third with fresh oxygen prepared with the greatest care. All three agreed absolutely to a tenth of a millimetre. Great pains were taken with these measurements on account of their disagreement with both Olszewski's and Estreicher's. The result obtained was  $p=171\cdot7$  mm.  $T=78^{\circ}08$ . Olszewski's and Estreicher's measurements were about 157 mm. at the same temperature. A very extraordinary faculty for being superheated was shown by the liquid nitrogen in these experiments. Although it was to all intents boiling, that is to say it was in actual ebullition, the temperature was  $0^{\circ}8$  above the true boiling-point. By dropping in pieces of copper wire or glass the temperature at once fell to the normal boiling-point, but if left the nitrogen rapidly superheated itself, and the temperature rose to exactly the same point as at first. It appears, therefore, that unless these liquefied gases are in a state of extremely rapid ebullition, they become superheated to a very considerable extent. This may possibly be the explanation of Estreicher's and Olszewski's results for vapour-pressures of oxygen being so much lower than the one I have obtained. It is true that Estreicher and Olszewski agree very well in their values at low pressures, but this may be quite easily accounted for, because they used the same thermometer, and because in my results the superheating is

## Vapour-Pressures of Nitrogen.

Temperature (absolute).	Pressure in mm.		
	Atmospheric.	Chemical.	Olszewski (Atmospheric).
77°	716·0	717·0	726·0
77·5	757·5	760·0	768·5
78	800·0	806·0	815·0
78·5	846·5	856·0	860·5
79	895·0	906·0	908·5
79·5	944·0	959·0	959·0
80	995·0	1013·0	1010·5
80·5	1048·0	1072·5	1065·5
81	1104·0	1130·5	1121·5
81·5	1163·0	1193·0	1180·0
82	1225·4	1258·0	1240·5
82·5	1290·0	1324·0	1304·0
83	1357·0	1386·0	1369·5
83·5	1426·0	1468·0	1438·0
84	1497·0	1544·5	1508·5
84·5	1570·5	1623·5	1582·0
85	1646·0	1705·5	1658·0
85·5	1725·0	1792·0	1737·0
86	1808·0	1880·0	1820·0
86·5	1895·0	1968·0	1904·5
87	1985·0	2062·0	1992·5
87·5	2076·0	2146·0	2081·0
88	2170·0	2256·0	2173·5
88·5	2267·0	2340·0	2268·0
89	2368·0	2465·0	2368·0
89·5	2472·5	2575·5	2472·0
90	2581·0	2686·0	2579·0
90·5	2694·0	2799·0	2688·0
91	2812·0	2916·5	2802·0
92·4	...	...	3125·0
94·1	...	...	3581·0
95·9	...	...	4088
97·6	...	...	4652
99·4	...	...	5274
101·2	...	...	5962
103·0	...	...	6717
104·9	...	...	7546
106·7	...	...	8644
108·6	...	...	9443
110·4	...	...	10520
112·3	...	...	11689
114·3	...	...	12956
116·2	...	...	14325
118·1	...	...	15801
120·1	...	...	17390
122	...	...	19097
124	...	...	20926

always exactly the same in the same apparatus, and a small quantity of gas bubbled through the liquid, such as Estreicher used, by no means lowers the temperature to the true boiling-point. In order to do this, a rapid current must be passed through, and this would naturally vitiate the vapour-pressure measurements. The values of the vapour-pressures are compared in the following table. In the first column are given

### Vapour-pressures of Oxygen.

Temperature (absolute).	Vapour-Pressure.		
	1. (B.)	2. (Ols.)	3. (E.)
62°	...	8·4	9·6
63	...	10·8	11·0
64	...	13·3	14·6
65	...	16·1	17·7
66	...	19·7	21·2
67	...	24·0	25·6
68	...	29·1	31·0
69	...	35·6	37·2
70	...	43·0	44·6
71	...	51·6	53·0
72	...	61·0	62·5
73	...	72·0	73·5
74	...	85·0	86·0
75	...	100·0	100·0
76	...	117·5	116·0
77·0	138·4	136·2	134·0
77·5	158·7	146·5	145·1
78·0	170·0	158·0	155·7
78·5	181·4	169·8	167·5
79·0	193·5	182·5	180·0
79·5	206·6	195·9	193·9
80·0	220·0	210·1	208·1
80·5	234·0	224·8	222·8
81·0	249·0	240·1	237·9
81·5	264·8	257·0	253·7
82·0	281·8	274·0	270·0
82·5	299·5	292·1	287·5
83·0	319·2	311·7	305·3
83·5	338·6	332·0	323·3
84·0	359·0	353·5	342·3
84·5	380·5	376·4	362·0
85·0	401·8	401·7	382·9
85·5	424·6	427·0	404·6
86·0	449·0	454·0	427·4
86·5	475·5	482·0	451·7
87·0	503·0	510·5	477·0
87·5	530·5	540·5	506·5
88·0	560·0	571·6	538·6
88·5	590·0	604·7	571·5
89·0	621·5	639·9	608·8
89·5	653·6	676·6	646·5
90·0	687·5	714·2	685·0
90·5	725·5	753·2	725·5
91·0	761·5	794·0	766·0

those calculated from my measurements ; in the second and third those found by Olszewski and Estreicher. Those given as Estreicher's are obtained by giving weight to his intermediate points, as explained above.

The values of the vapour-pressures of oxygen and nitrogen were introduced into the equation  $r' \text{ gas} = r \times \frac{P_0}{P_n}$ , but were not found to satisfy it, nor does the introduction of a constant factor improve it, as may be seen from the subjoined table, the last column of which expresses the ratio  $\frac{r'}{r} / \frac{P_0}{P_n}$ .

T.	$r'$ .	$r$ .	$\frac{P_0}{P_n}$ .	$\frac{r'}{r}$	
80	.1364	.5004	.2174	.2725	1.254
82	.3089	1.090	.2240	.2832	1.264
84	.5835	1.959	.2322	.2979	1.283
86	1.092	3.505	.2388	.3116	1.305
88	2.290	7.065	.2480	.3241	1.307
90	8.806	24.97	.2560	.3525	1.377

There does not appear, therefore, to be any connexion between the ratio of the vapour-pressures and the composition of the gaseous phase in the distillation of oxygen and nitrogen at constant pressure ; it would be better, however, for this purpose to investigate the distillation at constant temperature, and this it is proposed to do.

I have to express my cordial thanks to Professor Ramsay, at whose suggestion the work was begun, and who has shown great personal interest during the investigation; and especially am I indebted to Dr. F. G. Donnan for the valuable help he has given me at various times.

University College, London,  
February 1900.

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LII. *On the Distribution of a Gas in an Electrical Field.*  
By GEORGE W. WALKER, B.A., A.R.C.Sc., Sir Isaac Newton Student in the University of Cambridge\*.

THIS paper forms part of an essay on the kinetic theory of gases, at which I have been working for some time. The essay will not be published for some time yet ; but on account of the interest of the above question it seems desirable to publish the results at which I have arrived.

\* Communicated by the Physical Society : read March 9, 1900.

For the sake of generality we shall suppose that the number of free positive atoms in unit volume is  $n_1$ , the number of free negative atoms  $n_2$ , and the number of molecules N. These are averages and do not imply that the atoms which constitute the set  $n_1$  are the same at every instant, but that we have reached a state in which the number of molecules which disintegrate is equal to the number formed by recombination. We shall regard the molecule as consisting of a pair of atoms in contact, each of mass  $m$  and radius  $a$ , and one carrying a positive charge  $e$ , and the other a negative charge  $-e$ .

We consider first the case in which the gas as a whole is at rest.

Let  $\chi$  be the electrical potential and R the resultant force at a point.

Then Boltzmann's extension of Maxwell's distribution law gives at once

$$\begin{aligned} n_1 &= N_1 e^{-h\epsilon\chi}, \quad n_2 = N_2 e^{+h\epsilon\chi}, \\ N &= -A \int_{+1}^{-1} \epsilon^{-2eah} \frac{\partial \chi}{\partial \nu} \cos \vartheta \delta \cos \vartheta \\ &= A \frac{\sinh 2eah \frac{\partial \chi}{\partial \nu}}{eah \frac{\partial \chi}{\partial \nu}}, \end{aligned}$$

where  $\cos \vartheta$  is the angle which the axis of a molecule makes with the direction of R, i. e.  $-\frac{\partial \chi}{\partial \nu}$ ;  $h$  is the usual constant in the kinetic theory and is inversely proportional to the temperature.

We shall first show that these distribution laws satisfy the conditions of hydrostatic equilibrium.

If  $p$  be the pressure we get

$$p = \frac{n_1}{h} + \frac{n_2}{h} + \frac{N}{h},$$

which is Dalton's law of partial pressures.

Consider for the moment that  $\chi$  depends only on one coordinate,  $x$ . Then we must have

$$\frac{\partial p}{\partial x} = X,$$

where  $X$  is the bodily force acting on all the atoms and molecules in unit volume.

For the free positive atoms

$$X_1 = -en_1 \frac{\partial \chi}{\partial x} = \frac{1}{h} \frac{\partial n_1}{\partial x}.$$

For the free negative atoms

$$X_2 = en_2 \frac{\partial \chi}{\partial x} = \frac{1}{h} \frac{\partial n_2}{\partial x}.$$

For the molecules

$$\begin{aligned} X_3 &= +A2ea \frac{\partial^2 \chi}{\partial x^2} \int_{-1}^{+1} \epsilon^{-2eak} \frac{\partial \chi}{\partial x} \cos \vartheta \cos \delta \cos \vartheta \\ &= \frac{1}{h} \frac{\partial N}{\partial x}. \end{aligned}$$

Thus the equation of hydrostatic equilibrium is identically satisfied.

Let  $\rho$  be the electrical density, then

$$\begin{aligned} \frac{\partial^2 \chi}{\partial x^2} &= -4\pi\rho, \\ \rho &= en_1 - en_2 - \frac{\partial I}{\partial x}, \end{aligned}$$

where  $I$  is the intensity of electrification due to the molecules. It is sufficient to retain only squares of  $ea$  in calculating  $I$ , and there is little difficulty in showing that

$$\frac{\partial I}{\partial x} = -\frac{4}{3} N_0 h a^2 e^2 \frac{\partial^2 \chi}{\partial x^2}$$

where  $N_0$  is the number of molecules in unit volume at a part of the field where  $\frac{\partial \chi}{\partial z}$  is zero.

Hence

$$\frac{\partial^2 \chi}{\partial x^2} = 4\pi e(N_2 e^{eh\chi} - N_1 e^{-h\chi}) - \frac{16\pi}{3} N_0 h a^2 e^2 \frac{\partial^2 \chi}{\partial x^2}.$$

In general the equation is

$$\left(1 + \frac{16\pi}{3} N_0 h a^2 e^2\right) \nabla^2 \chi = 4\pi e(N_2 e^{eh\chi} - N_1 e^{-h\chi}).$$

We see that the effect of the molecules is simply to increase the specific inductive capacity, so that

$$K = 1 + \frac{16\pi}{3} N_0 h a^2 e^2.$$

I do not propose to discuss this value of  $K$  here. Suffice it to say that with the usual estimates of  $N_0 h$  and  $a$  it gives very nearly Professor J. J. Thomson's value of  $e$  calculated

from the electrochemical equivalent.  $K$  for a gas is, however, so nearly 1 that we may take it as 1 without vitiating our results.

The equation for  $\chi$  is then

$$\nabla^2 \chi = 4\pi e(N_2 e^{eh\chi} - N_1 e^{-eh\chi}).$$

In this general form little can be done with the equation; but when  $\chi$  depends only on  $x$  we can obtain the complete integral

$$\frac{\partial^2 \chi}{\partial x^2} = 4\pi e(N_2 e^{eh\chi} - N_1 e^{-eh\chi}).$$

Multiply by  $\frac{\partial \chi}{\partial x}$  and integrate,

$$\left(\frac{\partial \chi}{\partial x}\right)^2 = \frac{8\pi}{h} \left\{ N_2 e^{eh\chi} + N_1 e^{-eh\chi} - B \right\}$$

where  $B$  is an arbitrary constant.

This may be rewritten

$$\left(\frac{\partial \chi}{\partial x}\right)^2 = \frac{8\pi}{h} \sqrt{N_1 N_2} \left\{ 2 \cosh(eh\chi + \alpha) - \frac{B}{\sqrt{N_1 N_2}} \right\},$$

where

$$e^{2\alpha} = \frac{N_2}{N_1}.$$

$$\text{Put } \cosh\left(\frac{eh\chi + \alpha}{2}\right) = y,$$

and we get

$$\left(\frac{dy}{dx}\right)^2 = 2\pi h e^2 \sqrt{N_1 N_2} \{1 - y^2\} \left\{ 2 + \frac{B}{\sqrt{N_1 N_2}} - 4y^2 \right\}.$$

$$\text{Thus } \cosh \frac{eh\chi + \alpha}{2} = \operatorname{sn}(\lambda x + \beta, k)$$

$$\text{where } \lambda^2 = 2\pi h e^2 \sqrt{N_1 N_2} \left\{ 2 + \frac{B}{\sqrt{N_1 N_2}} \right\}$$

$$k^2 = \frac{4}{2 + \frac{B}{\sqrt{N_1 N_2}}}, \quad \text{if } \frac{4}{2 + \frac{B}{\sqrt{N_1 N_2}}} < 1,$$

and  $\beta$  is an arbitrary constant.

$$\text{If } \frac{4}{2 + \frac{B}{\sqrt{N_1 N_2}}} \text{ is } > 1,$$

we get

$$\cosh \frac{eh\chi + \alpha}{2} = \frac{1}{\operatorname{sn}(\lambda x + \beta, k)};$$

where

$$\lambda^2 = 8\pi h e^2 \sqrt{N_1 N_2},$$

$$k^2 = \frac{B}{4 + \frac{\sqrt{N_1 N_2}}{2}}.$$

Before discussing the nature of the solution we shall consider the case when an electric current is passing. We shall suppose that the current is due to the bodily transference of the free atoms, while the molecules have practically no bodily motion.

Fixing our attention for the moment on the positive group :—

Let  $p_1$  be the pressure,  $\rho_1$  the density, so that  $p_1 = \frac{\rho_1}{hm}$ , and let  $u_1$  be the group velocity. Then the hydrodynamical equations are

$$\frac{\partial u_1}{\partial t} + u_1 \frac{\partial u_1}{\partial x} = -\frac{1}{hm} \frac{\partial \log \rho_1}{\partial x} - \frac{e}{m} \frac{\partial \chi}{\partial x}$$

and

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial}{\partial x} \rho_1 u_1 = 0.$$

For a steady state

$$\frac{\partial \rho_1}{\partial t} = 0 = \frac{\partial u_1}{\partial t}.$$

Hence

$$\rho_1 = m N_1 e^{-h \frac{mu_1^2}{2} - e\hbar\chi}$$

and

$$\rho_1 u_1 = B_1,$$

where  $N_1$  and  $B_1$  are constants.

Similarly for the negative atoms we have

$$\rho_2 = n N^{-h \frac{mu_2^2}{2} + e\hbar\chi},$$

$$\rho_2 u_2 = B_2.$$

Hence the electrical density at a point is

$$\frac{e}{m} (\rho_1 - \rho_2),$$

and the electrical current is

$$= \frac{e}{m} (\rho_1 u_1 - \rho_2 u_2) = \frac{e}{m} (B_1 - B_2) = \gamma \text{ say.}$$

If the group velocities are small compared with  $v_0$  the velocity of light the potential is given by

$$K \frac{\partial^2 \chi}{\partial x^2} = -4\pi \frac{e}{m} (\rho_1 - \rho_2).$$

Now  $u_1$  and  $u_2$  may be small compared with  $\frac{1}{\sqrt{hm}}$ , i.e. small compared with the velocity of sound, and still give large currents.

If this is so we have approximately

$$\rho_1 = m N_1 e^{-eh\chi} \left\{ 1 - \frac{hm}{2} \frac{B_1^2}{N_1^2 m^2} e^{2eh\chi} \right\},$$

$$\rho_2 = m N_2 e^{eh\chi} \left\{ 1 - \frac{hm}{2} \frac{B_2^2}{N_2^2 m^2} e^{-2eh\chi} \right\}.$$

Thus, taking K as 1,

$$\frac{\partial^2 \chi}{\partial x^2} = 4\pi e \left\{ \left( N_2 + \frac{h}{2m} \frac{B_1^2}{N_1} \right) e^{+eh\chi} - \left( N_1 + \frac{h}{2m} \frac{B_2^2}{N_2} \right) e^{-eh\chi} \right\},$$

which is an equation of the same form as before.

The solution is thus

$$\cosh \frac{eh\chi + \alpha}{2} = \frac{1}{\operatorname{sn}(\lambda x + \beta, k)}$$

where

$$\epsilon^{2\alpha} = \frac{N_2 + \frac{h}{2m} \frac{B_1^2}{N_1}}{N_1 + \frac{h}{2m} \frac{B_2^2}{N_2}},$$

$$\lambda^2 = 8\pi h e^2 \sqrt{N_1 N_2 \left( 1 + \frac{h}{2m} \frac{B_1^2}{N_1 N_2} \right) \left( 1 + \frac{h}{2m} \frac{B_2^2}{N_1 N_2} \right)},$$

$$k^2 = \frac{2 + \sqrt{N_1 N_2 \left( 1 + \frac{h}{2m} \frac{B_1^2}{N_1 N_2} \right) \left( 1 + \frac{h}{2m} \frac{B_2^2}{N_1 N_2} \right)}}{4}$$

The particular form of solution adopted depends on the values of the arbitrary constants introduced. When there is no potential and no current we have  $N_2 = N_1$ . Again, if we assert the condition that the total number of atoms, viz.  $(N_2 + N_1 + 2N_0) \times (\text{vol.})$  is constant, we may regard  $N_2$ ,  $N_1$ , and  $N_0$  as known.

Since the current is made up of two streams we cannot

determine  $B_1$  and  $B_2$  uniquely unless we impose some relation between  $B_1$  and  $B_2$ . The most likely seems  $B_1 = -B_2$ . If the potential is given at two points then  $\beta$  and  $B$  are determined.

For the general discussion of the solution we may then take the form

$$\cosh \frac{eh\chi + \alpha}{2} = \operatorname{sn}(\lambda x + \beta, k),$$

where  $\alpha, \lambda, \beta, k$  are supposed known. We get

$$\cosh eh\chi + \alpha = 2 \operatorname{sn}^2(\lambda x + \beta, k) - 1.$$

Now  $\cosh eh\chi + \alpha$  is proportional to the matter density of free atoms. Further the density of the molecules is a function of  $(\frac{\partial \chi}{\partial x})^2$ , and the first integral is

$$\begin{aligned} \left(\frac{\partial \chi}{\partial x}\right)^2 &= \frac{8\pi}{h} \sqrt{N_1 N_2 \left\{ 1 + \frac{h}{2m} \frac{B_1^2}{N_1 N_2} \right\} \left\{ 1 + \frac{h}{2m} \frac{B_2^2}{N_1 N_2} \right\}} \\ &\times \left\{ 2 \cosh eh\chi + \alpha - \sqrt{\frac{B}{N_1 N_2 \left( 1 + \frac{h}{2m} \frac{B_1^2}{N_1 N_2} \right) \left( 1 + \frac{h}{2m} \frac{B_2^2}{N_1 N_2} \right)}}} \right\}. \end{aligned}$$

Thus in general the matter density of the gas is periodic. The distance between points of equal density is given by  $d$  where

$$\lambda d = m\omega + m'\omega',$$

where  $\omega$  and  $\omega'$  are the complete periods of the elliptic functions and  $m$  and  $m'$  are the least integers which make  $d$  real.

$\operatorname{Sinh} eh\chi + \alpha$ , which is proportional to the electrical density, is also periodic in the same period. Where the function  $\operatorname{sinh} eh\chi + \alpha$  vanishes we have an equal number of free positive and negative atoms. At such a place there is most chance of recombination. It is probable that such recombination gives rise to luminosity. If the points of maximum matter density coincide with the points of least electrical density, then the above calculation would indicate that we should have very well defined planes of maximum luminosity.

The planes of minimum electrical and maximum matter density will not, however, in general coincide. Thus, though we should still have planes of maximum luminosity, they will not be so well defined.

These considerations suggest that we have something very closely related to the condition of things in a striated vacuum-tube.

In order to test this further, let us consider how the distance between these maxima planes varies as the constant  $B$  varies.

Suppose  $N_1 = N_2$ , and  $B_1 = -B_2$ ,  
so that the current

$$\gamma = \frac{2e}{m} B_1.$$

Our first integral takes the form

$$\left(\frac{\partial \chi}{\partial x}\right)^2 = \frac{8\pi}{h} N_1 \left\{ 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right\} \left[ 2 \cosh eh\chi - \frac{B}{\left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right) N_1} \right].$$

The least value which  $\cosh eh\chi$  can have is 1.

Suppose  $F$  the value of  $\frac{\partial \chi}{\partial x}$  where  $\chi = 0$ .

$$\therefore \frac{-B}{1 + \left(\frac{h}{2m} \frac{B_1^2}{N_1^2}\right) N_1} = \frac{hF^2}{8\pi N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)} - 2,$$

so that

$$2 + \frac{B}{N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)} = 4 - \frac{hF^2}{8\pi N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)}.$$

When  $F = 0$  the appropriate solution is

$$\cosh \frac{eh\chi}{2} = \coth \lambda x + \beta$$

where

$$\lambda^2 = 8\pi h e^2 N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right).$$

Here the distance  $d$  is infinite.

As  $F^2$  increases from 0 to  $\frac{32\pi N_1}{h} \left\{ 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right\}$

the proper form is

$$\cosh \frac{eh\chi}{2} = \frac{1}{\operatorname{sn}(\lambda x + \beta, k)},$$

where

$$\lambda^2 = 8\pi h e^2 N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right),$$

$$\frac{4 - \frac{hF^2}{8\pi N_1 \left(1 + \frac{h}{2m} \frac{B_1^2}{N_1^2}\right)}}{4} = 1 - \frac{hF^2}{32\pi N_1 \left(1 + \frac{h}{2m} \frac{N_1^2}{B_1^2}\right)};$$

$$\therefore k'^2 = \frac{hF^2}{32\pi N_1 \left( 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right)}.$$

For small values of  $k'$

$$d = \frac{1}{\lambda} 2 \log \frac{4}{k'},$$

$$\text{when } F^2 = \frac{32\pi N_1}{h} \left\{ 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right\}$$

$$\cosh \frac{eh\chi}{2} = \frac{1}{\sin \lambda x + \beta} \text{ (ordinary circular functions).}$$

$$\lambda^2 = 8\pi h e^2 N_1 \left( 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right),$$

and

$$d = \frac{\pi}{\lambda}. \quad (\text{This is the least value of } d.)$$

From

$$F^2 = \frac{32\pi N_1}{h} \left( 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right) \text{ to } \infty$$

we get

$$\cosh \frac{eh\chi}{2} = \frac{1}{k'} \frac{dn\lambda x + \beta, k}{\sin \lambda x + \beta, k}$$

where

$$\lambda^2 = 8\pi h e^2 N_1 \left\{ 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right\} k'^2$$

and

$$k^2 = 1 - \frac{32\pi N_1}{h} \frac{\left\{ 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right\}}{F^2}$$

$$k'^2 = \frac{32\pi N_1}{h} \frac{\left\{ 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right\}}{F^2}$$

and if  $k'$  is small,

$$d = \frac{1 \times F}{16\pi N_1 e \left( 1 + \frac{h}{2m} \frac{B_1^2}{N_1^2} \right)} 2 \log \frac{4}{k'}.$$

Now Goldstein (Wied. *Anh.* xv. p. 277, 1883) finds that  $d$  is very nearly inversely proportional to the density, while Mr. R. S. Willoughs (Cav. Lab.) finds that above a certain strength of current the distance  $d$  diminishes as the current increases.  $N_1$  will be proportional to the density multiplied by some function of  $F$ , so that the formula for  $d$  will agree

fairly well with these experimental results if  $F^2$  lies between  $\frac{32\pi N_1}{h} \left\{ 1 + \frac{h}{2m N_1^2} B_1^2 \right\}$  and  $\infty$ .

The distance between the striæ depends on the diameter of the discharge-tube. It is possible that the solution of the general differential equation for  $\chi$  would lead to this, but it seems hopeless to attack the equation for two dimensions.

Another interesting deduction from the solution above, which has been verified experimentally since I made the calculation, is that while  $\frac{\partial \chi}{\partial x}$  is periodic in the striæ the potential  $\chi$  is not periodic.

The equation  $\cosh \frac{eh\chi + \alpha}{2} = \operatorname{sn}(\lambda x + \beta, k)$  may be transformed into

$$\sin \psi = \mu \operatorname{sn}(v, k)*,$$

where       $\psi$  is a linear function of  $\chi$ ,  
 $v$     "    "    "    "     $x$ ,  
 $\mu$  some constant,  
 $k$  some modulus.

Now this equation is just of the same form as that for the motion of a simple pendulum under gravity,  $\psi$  being the angle, and  $v$  the time, and we know that when the pendulum makes complete revolutions it is possible to express  $\psi$  as equal to  $\mu v$  and a series of periodic terms.

Thus,  $\chi$  in general is a linear function of  $x$  and a series of periodic terms.

$\chi$  must be real, and the series convergent. This will depend on the particular circumstances. That the series must converge to zero in one case is obvious, for if there are no free atoms  $\chi = Ax + B$  is a complete solution of the equation.

Further,  $\frac{\partial \chi}{\partial x}$  is periodic, although  $\chi$  is not so.

I understand that from measurements of  $\chi$  in the striæ,  $\chi$  is just of the nature we have found, while Mr. H. A. Wilson, at the Cavendish Laboratory, finds that  $\frac{\partial \chi}{\partial x}$  is periodic.

\* In the equation  $\frac{\partial^2 \chi}{\partial x^2} = 8\pi e \sqrt{N_1 N_2} \sinh(eh\chi + \alpha)$  put

$$eh\chi + \alpha = i\psi, \\ x = it;$$

and we get

$$\frac{\partial^2 \psi}{\partial t^2} = -8\pi e^2 h \sqrt{N_1 N_2} \sin \psi,$$

which is the equation of motion of a simple pendulum.

LIII. *Remarks upon the Law of Complete Radiation.*

By Lord RAYLEIGH, F.R.S.\*

**B**Y complete radiation I mean the radiation from an ideally black body, which according to Stewart † and Kirchhoff is a definite function of the absolute temperature  $\theta$  and the wave-length  $\lambda$ . Arguments of (in my opinion ‡) considerable weight have been brought forward by Boltzmann and W. Wien leading to the conclusion that the function is of the form

$$\theta^5 \phi(\theta\lambda) d\lambda, \quad \dots \dots \dots \quad (1)$$

expressive of the energy in that part of the spectrum which lies between  $\lambda$  and  $\lambda + d\lambda$ . A further specialization by determining the form of the function  $\phi$  was attempted later §. Wien concludes that the actual law is

$$c_1 \lambda^{-5} e^{-c_2/\lambda\theta} d\lambda, \quad \dots \dots \dots \quad (2)$$

in which  $c_1$  and  $c_2$  are constants, but viewed from the theoretical side the result appears to me to be little more than a conjecture. It is, however, supported upon general thermodynamic grounds by Planck ||.

Upon the experimental side, Wien's law (2) has met with important confirmation. Paschen finds that his observations are well represented, if he takes

$$c_2 = 14,455,$$

$\theta$  being measured in centigrade degrees and  $\lambda$  in thousandths of a millimetre ( $\mu$ ). Nevertheless, the law seems rather difficult of acceptance, especially the implication that as the temperature is raised, the radiation of given wave-length approaches a limit. It is true that for visible rays the limit is out of range. But if we take  $\lambda = 60\mu$ , as (according to the remarkable researches of Rubens) for the rays selected by reflexion at surfaces of Sylvin, we see that for temperatures over  $1000^\circ$  (absolute) there would be but little further increase of radiation.

The question is one to be settled by experiment; but in the meantime I venture to suggest a modification of (2), which appears to me more probable *à priori*. Speculation upon this subject is hampered by the difficulties which attend the Boltzmann - Maxwell doctrine of the partition of energy. According to this doctrine every mode of vibration should be

\* Communicated by the Author.

† Stewart's work appears to be insufficiently recognized upon the Continent.

‡ Phil. Mag. vol. xlv. p. 522 (1898).

§ Wied. Ann. vol. lviii. p. 632 (1896).

|| Wied. Ann. vol. i. p. 74 (1900).

alike favoured; and although for some reason not yet explained the doctrine fails in general, it seems possible that it may apply to the graver modes. Let us consider in illustration the case of a stretched string vibrating transversely. According to the Boltzmann-Maxwell law the energy should be equally divided among all the modes, whose frequencies are as 1, 2, 3, . . . . Hence if  $k$  be the reciprocal of  $\lambda$ , representing the frequency, the energy between the limits  $k$  and  $k+dk$  is (when  $k$  is large enough) represented by  $dk$  simply.

When we pass from one dimension to three dimensions, and consider for example the vibrations of a cubical mass of air, we have ('Theory of Sound,' § 267) as the equation for  $k^2$ ,

$$k^2 = p^2 + q^2 + r^2,$$

where  $p, q, r$  are integers representing the number of subdivisions in the three directions. If we regard  $p, q, r$  as the coordinates of points forming a cubic array,  $k$  is the distance of any point from the origin. Accordingly the number of points for which  $k$  lies between  $k$  and  $k+dk$ , proportional to the volume of the corresponding spherical shell, may be represented by  $k^2 dk$ , and this expresses the distribution of energy according to the Boltzmann-Maxwell law, so far as regards the wave-length or frequency. If we apply this result to radiation, we shall have, since the energy in each mode is proportional to  $\theta$ ,

$$\theta k^2 dk, \dots \dots \dots \dots \quad (3)$$

or, if we prefer it,

$$\theta \lambda^{-4} d\lambda. \dots \dots \dots \dots \quad (4)$$

It may be regarded as some confirmation of the suitability of (4) that it is of the prescribed form (1).

The suggestion is that (4) rather than, as according to (2),

$$\lambda^{-5} d\lambda \dots \dots \dots \dots \quad (5)$$

may be the proper form when  $\lambda\theta$  is great. If we introduce the exponential factor, the complete expression will be

$$c_1 \theta \lambda^{-4} e^{-c_2 \lambda \theta} d\lambda. \dots \dots \dots \dots \quad (6)$$

If, as is probably to be preferred, we make  $k$  the independent variable, (6) becomes

$$c_1 \theta k^2 e^{-c_2 k / \theta} dk. \dots \dots \dots \dots \quad (7)$$

Whether (6) represents the facts of observation as well as (2) I am not in a position to say. It is to be hoped that the question may soon receive an answer at the hands of the distinguished experimenters who have been occupied with this subject.

LIV. *Some Observations in reply to the Paper of Prof. C. G. Knott "On Swan's Prism Photometer, etc."* By O. LUMMER and E. BRODHUN \*.

UNDER the title "On Swan's Prism-Photometer, commonly called Lummer and Brodhun's Photometer," Prof. C. G. Knott calls attention, in the January number of this periodical, to the fact that Swan had already, in 1859, "invented, described, constructed, and used" the photometer afterwards "re-invented" by us. The description given by Swan of his photometer-cube at that time is also reprinted.

May we be permitted to offer some observations correcting certain points in the above-named paper which seem to us to be misleading?

It is, first of all, certainly much to be regretted that this publication has been delayed until now, although Prof. Knott says the Swan photometer has been "familiar to all officially connected with the Edinburgh University Physical Laboratory for some years past."

Now, however, that Mr. Swan's precedence in the field is brought to our attention after this long interval, we desire to be among the first to acknowledge it. But the statement that the photometer which we introduced into the technical world is nothing more than a re-invention of Swan's photometer seems equally unfair to us.

Fig. 1.



On the basis of theoretical considerations we formulated the conditions necessary for a "Gleichheits-Photometer" of the greatest possible sensitiveness. Following these in our preliminary paper †, only that photometer-cube was described which fulfilled the theoretical requirements of an ideal "grease-spot" (fig. 1). This preliminary paper was followed, however, by our "Photometrische Untersuchungen" ‡, in which the advantages and disadvantages of the various possible

\* Communicated by the Authors.

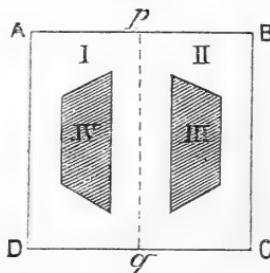
† *Zeitschrift f. Instrkde*, ix. pp. 23-25 (1889).

‡ *Ibid.* ix. pp. 41-50 (1889).

prism combinations were discussed. Among these is to be found the one which, as we now know, was invented by Swan forty-one years ago. This form was in our opinion, however, imperfect, and unsuited to technical requirements for the following reasons:—Apart from the fact that the balsam spot is not perfectly transparent, its edges do not afford that extreme sharpness which can be attained by ground surfaces, and they deteriorate by continually drying up. In consequence of this the balsam-spot cube, as well as some of the other prism-combinations perhaps superior to it, has never been recommended by us, and we doubt whether any considerable number have found their way into practical use in technical industry. Should photometers with balsam cubes, nevertheless, be now in use, they should of course be called Swan's photometers. But let us not forget that only with the most imperfect of all our described forms does the cube of Swan coincide, and the coincidence only extends to our "Gleichheit's" principle\*.

But we did not stop with the "Gleichheits-Würfel;" we have also constructed a prism-combination which not only satisfies all the conditions of the "Gleichheits" principle, but also allows the more sensitive "contrast-principle" †, first

Fig. 2.



worked out by us, to be realized. The construction of this prism combination with the help of a sand-blast is described in our paper, "Photom. Untersuchungen I.," under cube No. 5. Its field has commonly the appearance indicated in fig. 2. The different field-sections (I.—IV.) are separated

\* It may be remarked here that the cube form had been already used earlier by Fuchs for photometrical purposes, as mentioned in our paper. As criterion he used the disappearance of the interference-bands, which arise in the thin air-layer between the two prisms near the limit of total reflexion, and which are complementary to each other in reflected and refracted light.

† Photom. Untersuchungen, ii.: "Lichtmessung durch Schätzung gleicher Helligkeitsunterschiede (Kontrastphotometer)". *Zeitschrift f. Instrukte*, ix. pp. 461–465 (1889).

from each other by hair sharp edges, which disappear completely, so that the whole field ABCD looks like a uniform, diffusely illuminated surface. But as soon as one introduces thin glass plates at proper points in front of the two illuminated sides of the cube the "principle of contrast" is added to the "principle of equality." The fields I. and II. are of uniform intensity, in consequence of which their separating-edge  $pq$  disappears; the fields III. and IV. have another intensity, but the difference between I. and IV. being the same as the difference between II. and III., they show equal contrast.

In the treatise\* entitled "Die photometrischen Apparate der Reichsanstalt für den technischen Gebrauch," our photometer supplied with this "Gleichheits and Contrast-Würfel" is described and illustrated in the form in which it is constructed for technical use according to our designs by the Berlin firm, Franz Schmidt and Haensch. Whoever compares this photometer with Swan's prism-photometer will with an impartial judgment hardly agree with Prof. Knott when he exclaims, with reference to our photometer, "Let us now, who know its value, not forget that it is 'Swan's' photometer."

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**LV. Thermal Radiation in Absolute Measure.** By J. T. BOTTOMLEY, M.A., D.Sc., F.R.S., and J. C. BEATTIE, D.Sc., F.R.S.E.†

THE experiments‡ described in the following paper form a continuation of researches on thermal radiation by one of the present authors, the results of which have been communicated to the Royal Society from time to time since 1884 §. The main object of the present experiments was to push forward the inquiry as to the amount, and the relative quality,

\* Photom. Untersuchungen, iv.: *Zeitschrift f. Instrukte*, xii. pp. 41–50 (1892).

† Communicated by Lord Kelvin; having been read before the Royal Society, Feb. 1, 1900.

‡ The experimental results of the paper were obtained two years ago. Various circumstances have prevented earlier publication; and it was originally intended to carry the investigation further before publishing. Want of opportunity, however, makes this difficult for the present; and we therefore deem it advisable to put our results on record just now, as they stand. The present investigation, as well as the former work referred to in the text above, has been assisted by grants from the Government Grant Fund.

§ "On Thermal Radiation in Absolute Measure," J. T. Bottomley, Roy. Soc. Proc. and Phil. Trans. 1884–1893.

of the radiation from surfaces of various kinds in high vacuum.

When a body is maintained at a high temperature the total radiation from its surface depends, other things being the same, on the temperature and on the character of the radiating surface. With a given temperature the total radiation, consisting of thermal, luminous, and actinic rays, seems to depend on the nature and on the ultimate texture of the radiating surface; and the proportion in which vibrations of longer and shorter period are present seems to be governed by the coarseness or fineness of the structure of the surface at which the rays take their origin.

Very little progress has yet been made towards an investigation of the question just referred to; and the results of our experiments are intended to be a contribution in this direction.

In a former paper \* by one of us the loss of heat in vacuum from the metallic surface of platinum wires was determined; and Schleiermacher † has compared the loss from bright platinum wires and from platinum wires whose surface was coated thinly with black oxide of copper. Further experiments on this part of the subject seemed highly desirable, and were therefore undertaken by us.

The radiating body was a platinum wire. The way in which it was mounted is shown in figs. 1 and 2‡. The platinum wire, *a b*, is held, stretched between two spiral springs, in a glass tube. The outer ends of the spiral springs terminate in loops; and two pieces of glass rod, which are passed into tubes *c c*, *c' c'* (see figure), pass through the loops, so that the springs pull on these glass rods. After the rods have been passed into their places, the ends of the tubes *c c*, *c' c'* are closed up, except one, which is used for exhausting. Flexible electrodes are soldered to the loops of the spiral springs, and are silver-soldered to stout multiple platinum terminals; and by means of these, which are fused, with the help of some white enamel, into the glass at *d d*, the current is passed through the platinum wire. At *e e* platinum wires are brought through the sides of the tube, and serve as potential electrodes; and it is to keep the platinum wire *a b* in the middle of the length of the tube, and to avoid pulling unduly on the potential electrodes, that the two spiral springs, one at either end of the tube, are introduced.

\* Bottomley, Roy. Soc. Proc. 1887.

† Schleiermacher, Wied. Ann. vol. xxvi. 1885.

‡ The arrangement has been already described, J. T. Bottomley, Phil. Trans. vol. clxxviii. A, p. 448 (1887).

Two exactly similar tubes were employed, as shown in fig. 2. They were connected together by a side tube as shown; and by means of a branch tube, attached to this side tube and connected to a Sprengel pump, the air was withdrawn from both tubes at the same time. By this arrangement it was provided that the vacuum in the two tubes should be at all times precisely the same.

Fig. 1.

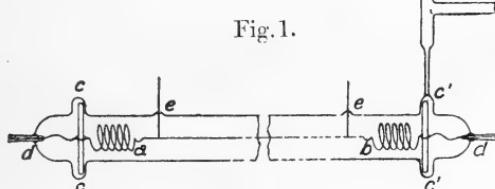
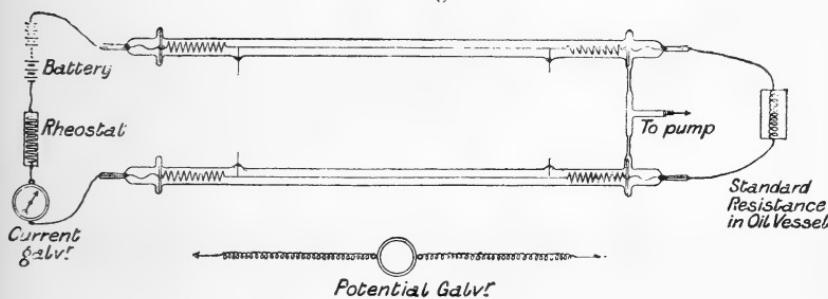


Fig. 2.



In one of the tubes the platinum wire was brightly polished and perfectly smooth just as it came from the maker's hands. The other tube contained a platinum wire cut from the same hank, but with the surface covered with an excessively fine coating of soot. The soot was put on by passing the wire carefully through the upper part of a clear paraffin-flame\*.

The usual arrangements were made for drying the vacuum of the tube, and of the pump, by means of phosphorus pentoxide; and the vacuum was measured by means of the Birmingham modification of the McLeod gauge.

The wires were heated, as in the former experiments, by

\* The texture of the soot depends greatly on the source from which it is obtained, and on the way in which it is applied to the wire. Some preliminary experiments have been made with various coatings of soot, and comparisons have been attempted between surfaces finely coated with soot, and surfaces prepared with platinum-black and with a fine coating of black oxide of copper chemically applied to the wire (*cf.* J. T. Bottomley, Phil. Trans. 1887, p. 449).

means of an electric current. Fig. 2 shows the electric connexions. A battery consisting of a sufficient number of secondary cells was employed ; and the current was controlled by means of suitable resistances, including a rheostat. In the experiments here described the platinum wires of the two tubes, the resistances, and the battery were all connected in series, so that the same current passed through all\*.

The current in the circuit was measured by means of a Kelvin ampere-gauge, and the difference of potentials at the two ends of each of the platinum wires was measured by means of a high-resistance reflecting-galvanometer.

This potential galvanometer had a resistance of about 5000 ohms, and it was possible to insert in the galvanometer-circuit an additional resistance of 10,000 ohms.

In order to ascertain the absolute value of the readings of the potential galvanometer, a standard coil of platinoid wire, whose resistance was known very accurately, was joined into the circuit, as shown in fig. 2. This resistance was of considerable length, and it was kept cool by being immersed in a bath of oil.

The following was the order of experimenting. The pressure in the tubes was first reduced as much as possible by means of the Sprengel pump ; then a very small current, practically unable to heat any part of the circuit, was sent through the two platinum wires and the standard coil, and the potential-difference between the two ends of each was determined. This gave the ratio of the resistance of each of the platinum wires to that of the standard coil, all being cold, and at the same temperature. The current from the battery of storage-cells was now suitably increased, and readings were taken in the following order :—The current passing was first read. Then the zero of the potential galvanometer was noted, and the deflexion of the potential galvanometer when connected to the two ends of the standard coil was observed. The electrodes of the potential galvanometer were next applied to one of the platinum wires, and the deflexion noted ; then the deflexion due to the second wire was observed. A second reading was taken from the first wire and also from the

\* In another set of experiments the platinum wires were joined in parallel, and, by means of two rheostats, one connected in series with each platinum wire, an attempt was made to regulate the current in each wire so that the temperatures in the two should be the same. This was found very difficult to carry out ; but it is intended to renew the attempt, and determine simultaneously the radiation from two wires with different surfaces, in the same vacuum, and at the same temperature.

second wire. Usually these pairs of readings were identical, or nearly so, as no reading was taken until after the strong current had been passing through the circuit for sufficient length of time to allow the temperature of the whole to become perfectly steady. Generally speaking, five minutes or more was allowed for this purpose. Lastly the current was again read, and the zero of the potential galvanometer noted.

The readings detailed above enabled us to calculate the current passing through each wire and the resistance in that wire. The length and cross-section of each of the platinum wires (practically identical) were also known. Thus the energy lost by radiation per square centimetre per second,  $C^2R/J\bar{S}$ , could be calculated ;  $C$  being the current,  $R$  the resistance and  $S$  the surface of the radiating wire, and  $J$  being the dynamical equivalent of heat, all in absolute measure.

The measurement of the electric resistance of the wires also enabled us to calculate the temperatures of the wires by means of the results of a separate determination of the electric resistances, at different temperatures, of the wires themselves.

In a former paper\*, the precautions and difficulties connected with the determination of change of resistances of platinum wires with temperature have been fully discussed. In the present case each platinum wire, after having been used in the radiation experiment, was wrapped round the bulb of an air thermometer † of special construction ; the bulb and wire were then packed in asbestos wool, and placed in the laminated copper heating-jacket described and figured in the paper just referred to. The jacket was heated by means of one of Fletcher's powerful "solid flame" burners, by means of which it could be kept for any length of time almost absolutely steady, at any temperature below the softening point of glass.

By means of stout copper electrodes the platinum wire was made one of the branches of a Wheatstone balance, and the electric resistance and temperature were simultaneously determined. A considerable number of readings between 15° C. and 350° C. were taken, and from these an empirical formula was constructed, or a curve drawn to represent the relation between temperature and pressure at all intermediate points.

\* J. T. Bottomley, Phil. Trans. 1887.

† J. T. Bottomley, "On a Practical Constant-volume Air Thermometer," Proc. Roy. Soc. Edin., December 19, 1887, and Phil. Mag., August 1888. This thermometer has proved perfectly satisfactory ; and the separation of the volume-gauge and pressure-gauge make it extremely convenient for applications of the kind referred to in the text.

In one respect, the determinations, an account of which is given in the present paper, are not perfectly satisfactory. The temperature of the circumambient air in all these experiments was from  $16^{\circ}$  to  $18^{\circ}$  Cent. ; but we have not been able to take account in a proper way of the temperature of the envelope enclosing the vacuous space in which the radiating wires were placed. In order to be able to see the condition of the wires, and in particular to observe their appearance when they became luminous, glass envelopes were used in these experiments ; and owing to the nature of the arrangements and the method of experimenting, it was not found possible to immerse the glass envelopes in a cooling bath. Consequently the glass became more or less heated during the experiments, and the heating was unequal in the cases of the bright wire and the sooted wire. It has already been pointed out\* that the proportion in which the radiations of longer period and shorter period are present in the total radiation depends on the radiating surface, other things being the same. In the case of the sooted wire, the quantity of long-period radiation is, in proportion, far in excess of that proceeding from a bright metallic polished surface. Consequently, with the same total electric energy supplied to both wires, the glass tube containing the sooted wire became much hotter than the tube containing the bright wire.

It has also been pointed out † that with a substance like glass, conducting badly and somewhat diathermanous, it is impossible to tell how much heat is returned to the radiating wire from the interior skin of the tube, which no doubt rises to a high temperature during the experiment. To a certain extent, therefore, the results which we have obtained must be considered as not affording results strictly comparable with those formerly obtained in which a metallic envelope cooled with water was used.

The absolute value of the radiation observed ought to be somewhat lower in amount than would have been found had the enclosing envelope been of metal and properly kept cool, and the disturbance from this cause must have been relatively greater in the case of the dull, than in the case of the bright, wire.

Experiments were made with platinum wires from three separate hanks. A pair of wires of equal length was taken in each case. One of these was left with its surface exactly as

\* Phil. Trans. 1887, A, p. 450.

† Loc. cit. p. 444.

it was on being taken from the hank ; the other was sooted. The two wires were then fixed in the glass tubes. The wires

are designated  $\overbrace{\text{Pt}_1, \text{Pt}_2}$ ,  $\overbrace{\text{Pt}_3, \text{Pt}_4}$ ,  $\overbrace{\text{Pt}_5, \text{Pt}_6}$ . The first of each pair is the bright wire ; the second is the sooted wire. The diameters of the wires are as follows :— $\text{Pt}_1$  and  $\text{Pt}_2$ , 0·0542 centim.,  $\text{Pt}_3$  and  $\text{Pt}_4$ , 0·025 centim. ;  $\text{Pt}_5$  and  $\text{Pt}_6$ , 0·015 centim.

In Tables I. and II. specimens are given of the results obtained, in the manner described above, by observation and calculation. The remainder of the results are embodied in the curves appended, which it is hoped will be found self-explanatory. At the head of each table the particulars as to the wires referred to in the table are given.

In the following tables, III., IV., V., the loss of heat per square centimetre of surface for the several pairs of wires, bright and sooted, at various temperatures, is compared ; and the ratio between the radiation from the sooted wire and the radiation from the bright wire is calculated. It will be seen that the numbers are in fair agreement. What may be the causes of divergence from exact agreement it is impossible to say at the present stage of the inquiry ; but it may be conjectured that part of it at least is due to the difficulty, or impossibility, of keeping the vacuum which surrounds the wires in these experiments unchanged. When the pressure is very low, the accession of the smallest quantity of gas to the surrounding space causes an enormous change in the rate of loss of heat, as has been shown in a previous part of this research, and as the temperature rises it is always found that the vacuum becomes deteriorated, owing to the expulsion of gas from the body of the wire itself. This gas must be removed by a fresh application of the pump, and, in fact, during the experiments the pump must be kept always at work. Thus the vacuum is incessantly changing ; and, moreover, as the indications of the McLeod gauge lag very much behind, it is not even possible to know the exact state of the pressure at the instant when it is desired to make an observation as to current passing and resistance. The consequence is that owing to the constantly altering state of the vacuum an irregularity is introduced in the loss of heat, and the irregularity tells more in the case of small wires than in the case of larger sizes.

In the case of the bright wire,  $\text{Pt}_5$ , the loss of heat was somewhat abnormal. It is probable that the surface was lacking in polish.

It will be seen that the loss from the sooted platinum wires

is about four to five times that from the bright wires at the same temperature. In the paper of 1894, already referred to, the radiation from a very brightly polished and burnished silvered copper globe, and that from the same globe sooted, were determined. The highest temperature reached was about  $230^{\circ}\text{C}.$ , and in that case the sooted globe lost about ten times as much heat as the silvered globe under the same circumstances. When the silvered globe had become tarnished, the radiation from its surface was so much increased that the loss from the sooted globe was only three times that from the tarnished silver.

TABLE I.—May 18, 1897. Two Platinum Wires  $\text{Pt}_1$  and  $\text{Pt}_2$ , length 42.55 cm., diameter 0.0542 cm., from the same hank of wire.  $\text{Pt}_1$  left with bright surface,  $\text{Pt}_2$  thinly sooted.

Current in Amperes.	$\text{Pt}_1$ .			$\text{Pt}_2$ .			Pressure in millimetres.
	Resist- ance in ohms.	Temp.	Thermal Energy lost per square centimetre per second.	Resist- ance in ohms.	Temp.	Thermal Energy lost per square centimetre per second.	
0.023	0.192	17	$0.033 \times 10^{-4}$	0.188	17	$0.0329 \times 10^{-4}$	0.00025
0.276	0.208	33	5.198	0.198	26	4.952	0.00025
0.552	0.259	89	25.98	0.209	36	20.96	0.00045
0.695	0.292	130	46.52	0.220	51	35.02	0.00045
0.940	0.337	185	97.97	0.237	71	69.90	0.00045
1.430	0.415	295	279.80	0.271	109	183.1	0.00045
1.937	0.484	453	599.5	0.317	167	393.0	0.00060
2.691	0.570	623	1371.0	0.377	249	912.2	0.00050
3.003	0.599	743	1776.0	0.398	280	1184.0	0.00060
3.770	.....	.....	.....	0.437	343	2055.0	0.00500*
4.446	.....	.....	.....	0.476	414	3106.0	0.00360
5.200	.....	.....	.....	0.515	496	4517.0	0.00320
6.604	.....	.....	.....	0.566	643	8166.0	0.00250

\* Owing to increase in the pressure, the emission here must be considerably increased by convection.

TABLE II.—June 17, 1897. Two Platinum Wires, Pt<sub>3</sub> and Pt<sub>4</sub>, length 39·2 cm., diameter 0·025 cm., from the same hank of wire. Pt<sub>3</sub> bright, Pt<sub>4</sub> sooted.

Current in amperes.	Pt <sub>3</sub> .			Pt <sub>4</sub> .			Pressure in millimetres.
	Resist- ance in ohms.	Temp.	Thermal Energy lost per square centimetre per second.	Resist- ance in ohms.	Temp.	Thermal Energy lost per square centimetre per second.	
0·0245	1·94	15	$0\cdot9004 \times 10^{-4}$	1·94	15	$0\cdot9004 \times 10^{-4}$	0·00040
0·0819	2·03	41	10·53	1·984	26	10·29	0·00010
0·1638	2·27	120	48·09	2·050	47	42·52	0·00025
0·2348	2·466	190	105·1	2·134	74	89·00	0·00033
0·3003	2·602	243	181·4	2·224	109	155·1	0·00025
0·3822	2·781	318	314·2	2·314	135	261·5	0·00025
0·4586	2·900	377	473·1	2·399	166	390·2	0·00025
0·5405	3·039	445	686·7	2·492	200	563·0	0·00025
0·6470	3·196	538	1034·0	2·610	245	844·7	0·00016
0·8479	3·418	719	1902·0	2·788	321	1552·0	0·00025
1·0230	.....	.....	.....	2·919	383	2362·0	0·00050
1·1696	.....	.....	.....	3·033	442	3209·0	0·00130
1·462	.....	.....	.....	3·228	560	5338·0	0·0019
1·608	.....	.....	.....	3·331	687	6658·0	0·0025
1·754	.....	.....	.....	3·424	726	8149·0	0·0023

Tables III., IV., V., comparing the Amount of Thermal Energy lost per sq. centim. per second by each of two precisely similar Platinum Wires at the same temperature, one of the wires having a Bright Metallic Surface and the other being Lightly Sooted.

TABLE III.  
Pt<sub>1</sub> and Pt<sub>2</sub>. Diameter of Wire, 0·0542 cm.

Temperature.	Energy lost by bright wire.	Energy lost by sooted wire.	Ratio sooted/bright.
200	1·1	5·3	4·8
250	1·8	8·9	4·9
300	2·7	12·8	4·7
350	3·8	19·8	5·2
400	4·9	26·1	5·3
450	6·2	33·3	5·4
500	7·9	42·0	5·3
550	10·0	50·0	5·0
600	11·9	58·5	4·9
650	13·8	68·7	5·0

TABLE IV.  
 $\text{Pt}_3$  and  $\text{Pt}_4$ . Diameter of Wire, 0·025 cm.

Temperature.	Energy lost by bright wire.	Energy lost by sooted wire.	Ratio sooted/bright.
150	0·7	3·3	4·71
200	1·1	5·9	5·4
250	1·8	9·2	5·1
300	2·7	13·5	5·0
350	3·7	18·6	5·0
400	4·9	24·1	4·9
450	6·4	31·0	4·9
500	8·0	38·7	4·84
550	10·1	46·5	4·6
600	12·1	54·0	4·5
650	15·9	67·5	4·2
750	21·8	86·5	4·0

TABLE V.  
 $\text{Pt}_5$  and  $\text{Pt}_6$ . Diameter of Wire, 0·015 cm.

Temperature.	Energy lost by bright wire.	Energy lost by sooted wire.	Ratio sooted/bright.
200	1·0	4·5	4·5
250	1·3	5·7	4·4
300	2·0	8·7	4·35
350	3·2	13·0	4·06
400	4·7	18·8	4·0
450	7·0	27·4	3·9
500	9·9	37·8	3·8
550	14·9	57·0	3·8

Fig. 3.—Curves showing emission of heat from  $\text{Pt}_1$  (bright) and  $\text{Pt}_2$  (sooted), from the same hank of wire, diameter 0.0542 centim., at various temperatures.

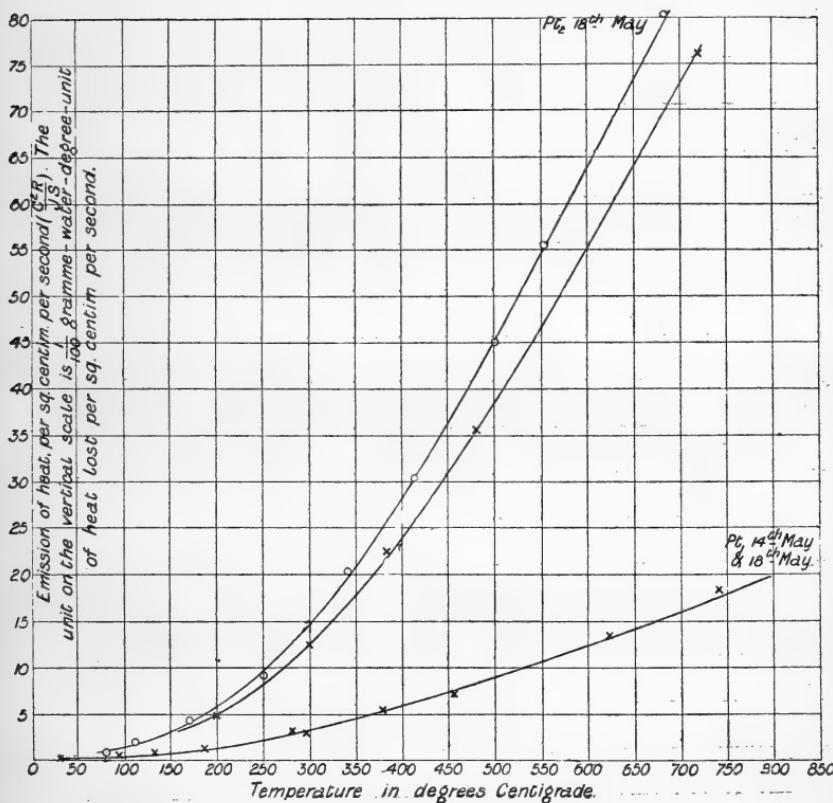


Fig. 4. — Curves showing emission of heat from Pt<sub>3</sub> (bright) and Pt<sub>4</sub> (sooted), from the same hank of wire, diameter 0·025 centim., at various temperatures.

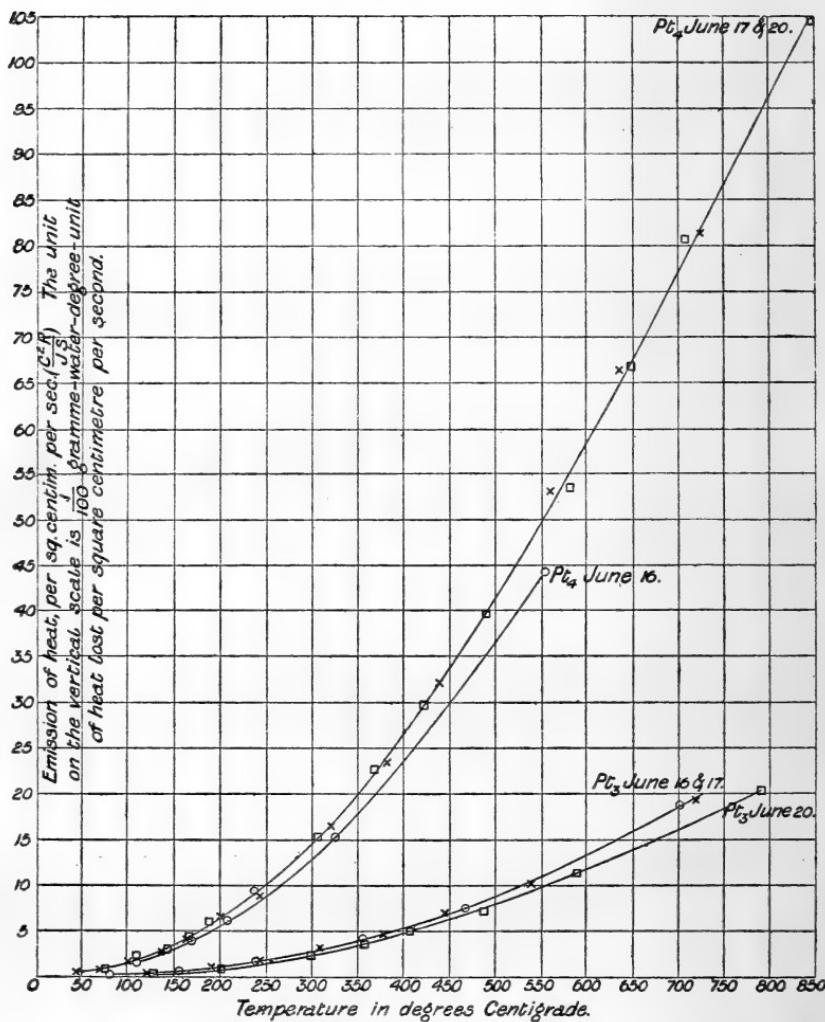


Fig. 5.—Curves showing emission of heat from  $\text{Pt}_5$  (bright) and  $\text{Pt}_6$  (sooted), from the same hank of wire, diameter 0.015 centim., at various temperatures.

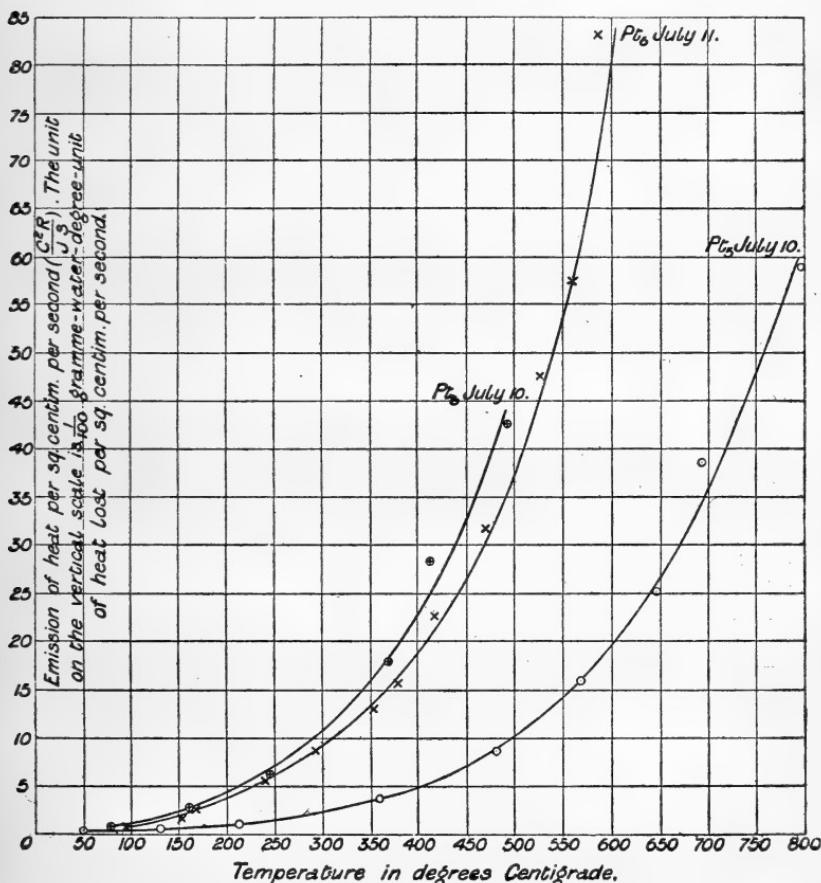


Fig. 6.—Emission of heat from three bright platinum wires,  $Pt_1$ ,  $Pt_3$ ,  $Pt_5$ , of different diameters as indicated.

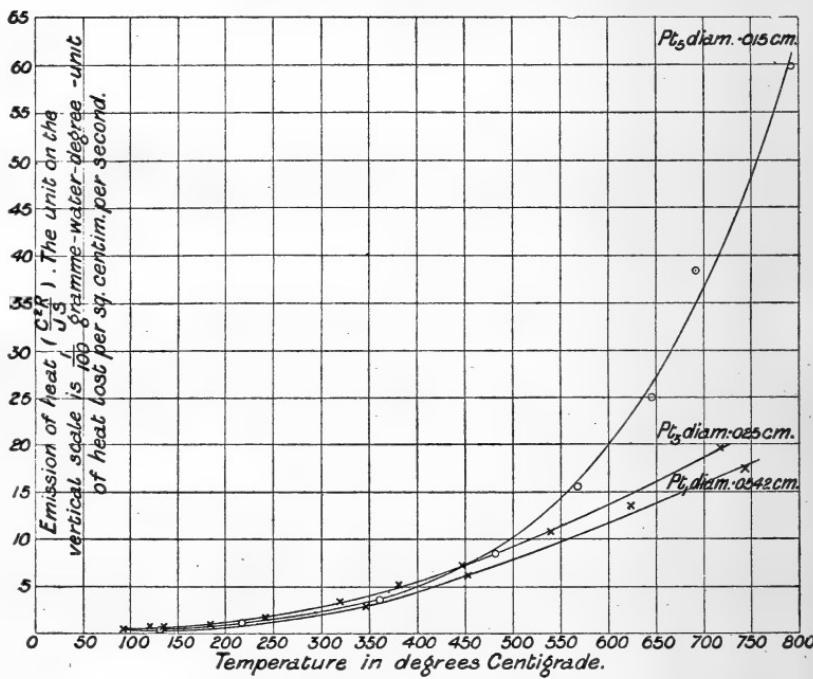
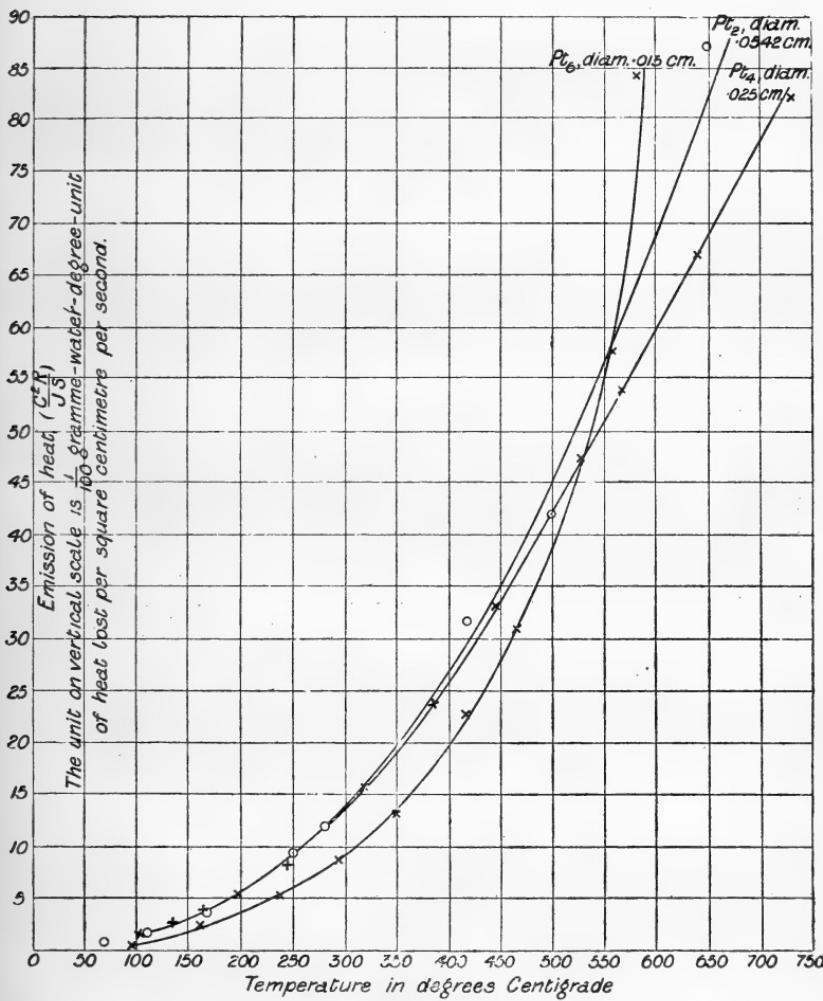


Fig. 7.—Emission of heat from three sooted platinum wires,  $Pt_2$ ,  $Pt_4$ ,  $Pt_6$ , of different diameters as indicated.



*LVI. On the Influence of Proximity of Mass upon Electric Conduction-resistance.* By Dr. G. GORE, F.R.S.\*

IN a previous research on the Influence of Proximity of Substances upon Voltaic action (Phil. Mag. June 1897), I have shown that the presence of a mass of a heavy substance near one of the electrodes of a voltaic cell alters its electro-motive force; and as I have since then made a very tedious research to determine whether the same influence affects the electric conduction-resistance of metal wires, I beg leave to describe, in the briefest possible form, the general arrangement adopted for testing the question.

The apparatus employed consisted of an Elliott's differential galvanometer ("No. 96" in their catalogue), having a resistance of "3140 ohms" in each coil, and a six-inch cube of lead weighing nearly eighty pounds divided in two halves vertically, and having spaces cut out of its opposing surfaces to receive a coil and thermometer. Two coils were employed, each being about  $\frac{3}{4}$  inch diameter and  $2\frac{1}{2}$  inches long, the insulated copper wire upon each being .002 inch diameter, and having a resistance of "7432 ohms at  $15^{\circ}5$  C." Two similar and very sensitive thermometers were also used, readable to a one-hundredth of a C. degree, and verified at Kew.

Sufficient uniformity of temperature of the coils and thermometers was secured by enclosing them in a nest of five wooden boxes with intervening layers of cotton-wool and sheets of brightly tinned iron, with layers of flannel outside; the inner box contained two smaller ones, 6 inches square and 3 inches apart, to contain the cube of lead, the comparison coils, and thermometers. The nest of boxes was placed in a carefully selected situation, so that the average temperatures of the thermometers when in the two small boxes were as nearly as possible alike.

Equal rates of transmission of temperature from the external atmosphere to the centres of the small boxes when the leaden cube was in place, so that each thermometer arrived at a maximum or a minimum at the same time, were ultimately secured by lining the entire surface of the empty box with plates of paraffin one inch thick.

The coils employed consisted of the pair of copper ones already mentioned; a second ditto about  $3\frac{1}{2}$  inches long, wire .003 inch diameter, and resistance about 350 ohms; a third pair about  $5\frac{1}{2}$  inches long, wire .003 inch diameter, and resistance about 350 ohms; and a fourth of aluminium wire,  $5\frac{1}{2}$  inches long and  $\frac{3}{4}$  inch diameter, wire .003 inch diameter, and resistance of about 1800 ohms. The covered wire upon all the coils was carefully insulated with paraffin.

\* Communicated by the Author.

The sources of voltaic current employed varied from a single couple to four hundred in series of small copper and zinc plates in a slightly acidified solution of sodic sulphate, the galvanometer being used differentially and the current divided in parallel between the coil in the lead and that in the paraffin-box. With the four hundred cells a considerable current passed.

The greatest care was taken to adjust the galvanometer to perfect neutrality with the full current passing, and to make each pair of coils perfectly equal in resistance when placed together in the centre of the space between the two small boxes and at exactly the same temperature.

After very numerous experiments extending over many months ; frequently exchanging the situations of the coils in the cube of lead and the paraffin-box ; making corrections for minute differences in the two thermometers and small changes in the galvanometer ; and in all cases taking the observations of conduction-resistance when the two coils were at exactly the same temperature in the two boxes, no perceptible difference could be detected in the resistance of either of the pair of coils by the influence of the lead : the influence of the lead, therefore, if any, must have been excessively minute. A single millimetre of movement of the reflected image upon the scale at a distance of one metre from the needles could easily be detected ; and the current from a single cell of the battery was quite sufficient to send the image rapidly off the scale when the galvanometer was used nondifferentially.

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*LVII. On the Damping of Galvanometer Needles.*

By MAURICE SOLOMON\*.

IT is well known that shortening the period of oscillation of a galvanometer-needle by increasing the strength of the magnetic controlling field decreases the *decrement*, or ratio of one complete swing to the next. It follows therefore that for a given initial amplitude of vibration a needle swinging in a strong controlling field will make a greater number of oscillations before coming to rest than when swinging in a weak field ; but since the time of each oscillation is less in the former case it does not follow that the time required for the amplitude to be reduced to a given fraction (say  $\frac{1}{m}$ ) of its initial value is greater with a strong than with a weak controlling field.

\* Communicated by the Physical Society : read March 9, 1900.

Examining the question theoretically, and making the usual assumption that the retarding forces are proportional to the first power of the velocity, one arrives at the conclusion that the time taken for the amplitude to become  $1/m$  of its initial value is independent of the strength of the controlling field, and so the time taken by the needle in coming to rest from a given initial deflection should be the same whether the period of vibration is long or short.

For, making the assumption stated above, we have as the equation of motion for a needle of magnetic moment  $M$ , and of moment of inertia  $I$ , swinging in a uniform magnetic field of strength  $H$ ,

$$I \frac{d^2\alpha}{dt^2} + N \frac{d\alpha}{dt} + HM \sin \alpha = 0,$$

where  $\alpha$  is the deflexion at time  $t$ , and  $N$  is the coefficient allowing for the *damping*, by which is meant *the resistance tending to destroy the motion of the needle*. This resistance is due to the viscosity of the air and of the suspension fibre, and also to the eddy-currents set up by the swinging needle in neighbouring metallic circuits. Of these retarding forces that due to the eddy-currents must be proportional to the first power of the velocity; but it is possible that those due to the viscosity of the air and the suspension fibre vary as some function of the velocity other than its first power.

When the angle of swing is small we may take  $\alpha$  instead of  $\sin \alpha$ , and if we put

and

$$N/I = 2n,$$

$$HM/I = p^2,$$

the above equation becomes

$$\frac{d^2\alpha}{dt^2} + 2n \frac{d\alpha}{dt} + p^2\alpha = 0.$$

This equation can easily be solved and gives for the periodic time reckoned either from one maximum deflexion to the next maximum deflexion on the same side, or, as the time between two successive crossings of the zero in the same direction,

$$t = \frac{2\pi}{\sqrt{p^2 - n^2}},$$

and if  $\delta$  be the decrement, or ratio of one complete swing to the next, we obtain

$$\delta = e^{-\frac{n\pi}{\sqrt{p^2 - n^2}}},$$

so that the logarithm of the decrement to the base  $e$ , known as the *logarithmic decrement*, is

$$\lambda = \frac{n\pi}{\sqrt{p^2 - n^2}}.$$

The true periodic time,  $T$ , of the swinging system, that is to say the periodic time it would have if the damping forces were absent, is given by

$$T = t \frac{\pi}{\sqrt{\pi^2 + \lambda^2}}.$$

From the expressions above found for the observed periodic time  $t$  and the logarithmic decrement  $\lambda$ , we get

$$\frac{t}{\lambda} = \frac{2}{n} = \frac{4I}{N},$$

so that the ratio  $t/\lambda$  is independent of the strength  $H$  of the controlling field, and will remain constant when  $t$  is varied by altering this strength, provided  $I$  and  $N$  remain constant.

The time  $\tau$  for the reduction of the deflexion to  $\frac{1}{m}$  of its original value is given by

$$\tau = \frac{1}{2} \log_e m \frac{t}{\lambda},$$

and is therefore constant so long as  $t/\lambda$  is constant, or, consequently, so long as  $I$  and  $N$  remain constant.

With a view to testing the conclusion arrived at by the above reasoning, experiments have been made at the Central Technical College, beginning in 1891 and continued at intervals since that time, the results of which have shown a decided discrepancy between theory and experiment. The method adopted was to observe the periodic time and the corresponding decrement with different strengths of controlling field. Calculating out from these observations the values of the ratio  $t/\lambda$ , i.e. the ratio of the periodic time to the logarithmic decrement, showed that in most of the instruments tested the value of this ratio was not constant as indicated by theory. As examples of the results obtained, three sets of experiments on galvanometers of different types may be quoted.

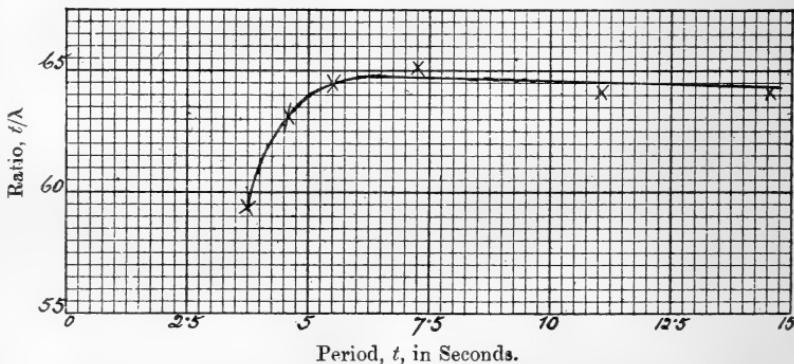
The first set of experiments was made by Mr. Seaman in 1891, on a Mudford's Thomson galvanometer similar to that illustrated in fig. 6 of Messrs. Ayrton, Mather, and Sumpner's paper on "Galvanometers" (Phil. Mag. July 1890, p. 70). The suspended system consists of an aluminium wire having small magnets affixed to the upper and lower ends, and the

mirror affixed at the centre. The mirror is enclosed in a small case with glass back and front so arranged that these glasses can be screwed nearer together or farther apart, thus enabling the space in which the mirror swings, and consequently the air damping, to be varied. A pair of coils is placed one behind and one before the upper set of magnets, and a similar pair before and behind the lower set, the coils being enclosed in ebonite boxes fitted into a brass frame. By thus placing the mirror outside, instead of at the centre of the coils, an improvement introduced into the Thomson galvanometer by Mr. Mudford, the coils may be wound practically to the centre and much valuable space utilized. The strength of the controlling field is varied by sliding a magnet up and down a vertical upright fixed to the top of the instrument case. As a result of these experiments Mr. Seaman found that the ratio  $t/\lambda$  increased as the period increased, becoming, however, nearly constant at long periods. The actual results are given in Table I., and plotted as a curve in fig. 1. This curve is plotted with the values of  $t$ , the observed period, as abscissæ, and the values of  $t/\lambda$  as ordinates, the values of  $t/\lambda$  being taken in preference to those of  $\lambda/t$ , as might appear more rational, because, as has been shown above, it is the ratio  $t/\lambda$  that occurs in the expression for the time of the reduction of the deflexion to  $1/m$  of its original value.

TABLE I.—Mudford's Thomson Galvanometer.

Period, $t$ , in seconds .....	3.75	4.63	5.46	7.24	11.06	14.55
Logarithmic decrement, $\lambda$ .....	0.0631	0.0734	0.0854	0.1112	0.1725	0.2268
Ratio, $t/\lambda$ .....	59.4	63.2	64.5	65.1	64.2	64.1

Fig. 1.



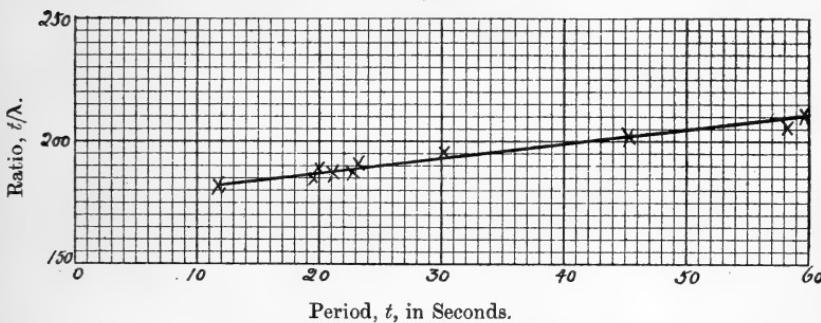
A series of experiments was made by Mr. Macquay in 1896 on a ballistic galvanometer, made by Messrs. White of

Glasgow to the designs of Messrs. T. & A. Gray, which is illustrated in figs. 11 and 12 of the paper above referred to. In this instrument there are a pair of long needles arranged to form an astatic combination, and each having one end sucked into and the other end pushed out of a coil, the four coils being enclosed in rectangular ebonite boxes. These needles are attached by an aluminium bridge to a vertical aluminium wire fastened at its upper end to the suspending fibre, and carrying at its lower end a pair of mirrors fastened back to back, the one being concave and the other plane, and also carrying at its lower end a small magnetic needle between a pair of auxiliary coils intended to be joined up in series with a battery and reversing-key and used as damping coils. The strength of the controlling field is varied by moving a magnet placed on the bench on which the instrument stands up to or away from the galvanometer. The results obtained showed a decided steady increase in the ratio  $t/\lambda$  with an increase of  $t$ . (See Table II. fig. 2.)

TABLE II.—Ballistic Galvanometer.

Period, $t$ , in seconds ...	11.8	19.6	20.0	21.1	22.9	23.1	30.1	45.6	58.2	59.7
Logarithmic decrement, $\lambda$ ...	0.0654	0.106	0.106	0.113	0.122	0.121	0.154	0.227	0.283	0.284
Ratio, $t/\lambda$ .....	180.8	185.0	188.6	186.8	187.0	190.8	195.3	200.6	205.5	210.3

Fig. 2.



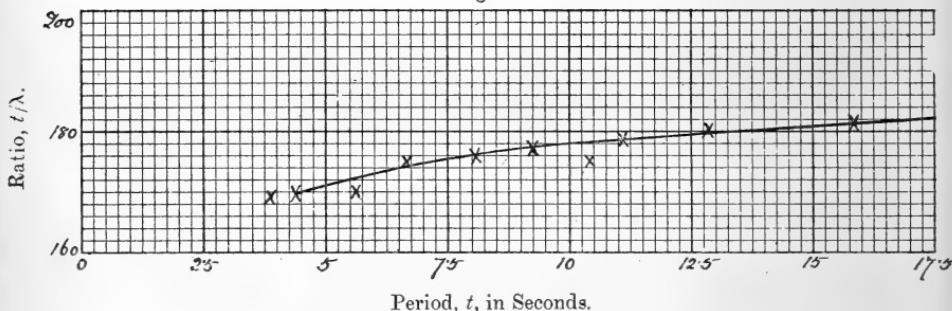
Finally, Mr. Taylor made some experiments in 1896 upon a Rosenthal galvanometer. The suspended system of this instrument is illustrated in fig. 10 of the paper previously referred to, and consists of an astatic pair of needles fastened below the mirror, each needle being bent into the shape of a horseshoe. One pole of each needle passes into the centre of a coil, whilst the other pole is on the outside of the coil, and the needles are therefore sucked into or pushed out of these coils by the action of the current. The results of these experiments showed an increase in the ratio  $t/\lambda$  as  $t$  increased,

the change being slightly more marked at the short periods. (See Table III. and fig. 3.)

TABLE III.—Rosenthal Galvanometer.

Period, $t$ , in	3.86	4.33	5.61	6.70	8.10	9.25	10.40	11.08	12.80	15.80	18.60
seconds ...											
Logarithmic	0.0228	0.0256	0.0330	0.0382	0.0459	0.0523	0.0597	0.0618	0.0709	0.0873	0.113
decrement, $\lambda$											
Ratio, $t/\lambda$ ...	169.5	169.3	170	175	176	177	175	179	180.5	181	182.5

Fig. 3.



Period,  $t$ , in Seconds.

These experiments (which have been selected from amongst the large number made at the Central Technical College as being typical) succeed in establishing the fact that the ratio  $t/\lambda$  does not remain constant when the strength of the controlling field is altered, but they do not explain why the conclusion derived from the theoretical equation is not borne out in practice. At the suggestion of Mr. Mather I made a series of experiments to find out if possible to what cause the variation in the ratio was due. It has been shown above that the ratio  $t/\lambda$  will remain constant when the strength of the controlling field is varied, provided that  $I$  and  $N$  remain constant.  $N$ , it is to be noticed, allows for the damping caused by the viscosity of the air and the suspension, and by the eddy-currents, and is therefore so far as the last cause is concerned a function of  $M$ , the magnetic moment of the swinging needle, and consequently will not remain constant if the strength of the controlling field affects the strength of the needle. We have then the following possible explanations of the variation of the ratio :—

1. *I may not be constant.*—This may occur through the controlling magnet deflecting the swinging system slightly from the vertical, and thus altering the axis of rotation : this is more likely to occur when the field is varied by moving the controlling magnet in a horizontal plane than when it is varied by moving the magnet up and down in a vertical plane passing through the needle.

2.  $N$  may not be constant.—This may occur in three ways:—
- i. The factor introduced by the air resistance may not be constant, the air resistance being possibly not proportional to the first power of the velocity.
  - ii. For the same reason it is possible that the factor introduced by the viscosity of the suspension may not be constant.
  - iii. The factor introduced by the eddy-current damping may not be constant. There are three causes which may make this factor vary.

In the first place, since the E.M.F. induced by the swinging needle is proportional to the first power of its velocity and to its strength, the damping effect of the eddy-currents will be proportional to the square of the strength of the swinging needle; and it is quite possible that altering the strength of the controlling field may alter the strength of the needle.

Secondly, if the galvanometer coils have a self-induction such that the reactance is not negligible, at the periods used, when compared with the resistance, the eddy-currents set up will not only lag behind the induced E.M.F., but will be to a certain extent choked out. And as these effects will be greater at the fast periods, the damping will be diminished at these periods, thus causing the ratio  $t/\lambda$  to increase as the period decreases.

Thirdly, it is possible that the eddy-currents will produce a rise in temperature sufficient to appreciably affect the resistance of the galvanometer coils. This will diminish the eddy-currents most at the short periods, thus producing an effect similar to that due to self-induction, namely an increase of  $t/\lambda$  as the period decreases.

To find out if possible which of the above was the true cause of the discrepancy between theory and experiment, it was decided to make some experiments in which the ratio  $t/\lambda$  was first determined for various strengths of controlling field for a needle swinging in a system in which the eddy-current damping was reduced to a minimum, if not entirely eliminated: and secondly for the same system but with considerable eddy-current damping introduced. In this way it would be possible to discover whether the effect was due to the eddy-currents or not.

Some preliminary trials showed that, to obtain satisfactory observations with vibrations of long period, it would be necessary to perform the experiments at night when there was comparative freedom from the disturbances due to traffic, since, although the galvanometer was placed on a stone

foundation-pillar, it was found impossible to get good readings when the traffic was at all frequent. The whole set of observations was therefore made between twelve and six on the morning of June 23rd, 1898. A sixty-ohm simple reflecting galvanometer was used with an astatic combination of four small needles affixed to a wire to the upper end of which the mirror was fastened, the whole being suspended by a single silk fibre. This system swung between the coils of the galvanometer, and as it had no mica vane the air damping was not great. As the coils were of fine wire, and the parts of the galvanometer nearly all of wood, the eddy-currents would be very small when the coils were on open circuit, and the damping in that case would be almost entirely due to the air resistance and the viscosity of the suspension. When, however, the galvanometer circuit was closed by short-circuiting the terminals, eddy-currents would be set up, and would introduce a considerable factor in the damping; so that if the alteration in the ratio  $t/\lambda$  is due to the factor introduced by the eddy-currents, it would be observable with the galvanometer circuit closed, but not with it open.

The determinations of the period were made by observing with a stop watch the time taken in executing several complete swings—from five or six when the period was long, to twenty when it was short. The time was read as the spot of light passed the zero of the galvanometer scale. Unfortunately in the experiments with a period of 16 seconds the true zero was about 25 divisions out, in such a direction as to cause the observed period to be too small. Had the amplitudes of the first and last swings used in determining the period been observed, it would be possible to make an accurate correction: as this was not done, it is only possible to make an approximate one, which will not, however, be far wrong, and which has been made in the results given in the table.

In observing the decrement when the period was long, the amplitudes of successive swings on both sides of the zero were observed. If these be  $a, b, c, d, e, \dots \&c.$ , we have

$$\text{Decrement} = \frac{a}{b} = \frac{b}{c} = \dots = \frac{a+b}{b+c} = \frac{b+c}{c+d} = \dots \&c.$$

By thus using  $\frac{a+b}{b+c}$  instead of  $\frac{a}{b}$  to calculate the decrement any zero error is eliminated. A specimen of the actual readings obtained in an observation of this type is appended.

Galvanometer-Circuit closed. Period 7.78 seconds.

Decrement—

$$(a) \frac{543}{482} = 1.126, \quad \frac{482}{431} = 1.119, \quad \frac{431}{383} = 1.126, \quad \frac{383}{341} = 1.122,$$

$$\frac{341}{305} = 1.117, \quad \frac{305}{272} = 1.121, \quad \frac{272}{242} = 1.125, \quad \frac{242}{217} = 1.115, \quad \frac{217}{193} = 1.125.$$

$$(b) \frac{566}{504} = 1.124, \quad \frac{504}{450} = 1.119, \quad \frac{450}{399} = 1.127, \quad \frac{399}{357} = 1.118,$$

$$\frac{357}{319} = 1.120, \quad \frac{319}{284} = 1.122, \quad \frac{284}{254} = 1.116, \quad \frac{254}{226} = 1.124, \quad \frac{226}{201} = 1.125.$$

Mean of above values = 1.121.

$$\text{Average decrement from observations } (a) = \sqrt[9]{\frac{543}{193}} = 1.120.$$

$$\text{, , , , } (b) = \sqrt[9]{\frac{566}{201}} = 1.122.$$

Mean decrement,  $\delta = 1.121$ .

$$\lambda = \log_e \delta = 0.114.$$

$$\text{Ratio, } t/\lambda = 68.1.$$

When the period was short, the spot of light moved too quickly for me to be able to read on both sides of the zero. For the two cases in which the period was 2.66 and 3.65 seconds respectively, I accordingly observed successive swings on the same side of the zero. We then have

$$\frac{a}{c} = \frac{a}{b} \cdot \frac{b}{c} = \delta^2.$$

Hence the values for  $\lambda$  are hardly so certain in these cases as in those in which the period was longer, especially as the spot of light moves so fast that it is more difficult to observe the deflexions accurately. A specimen of the readings of this type is given below.

Galvanometer-Circuit open. Period 3.65 seconds.

(Decrement)<sup>2</sup>—

$$(a) \frac{313}{288} = 1.087, \quad \frac{288}{262} = 1.097, \quad \frac{262}{240} = 1.090, \quad \frac{240}{218} = 1.100, \quad \frac{218}{199} = 1.092,$$

$$\frac{199}{183} = 1.090, \quad \frac{183}{166} = 1.101, \quad \frac{166}{151} = 1.099, \quad \frac{151}{138} = 1.093, \quad \frac{138}{124} = 1.112,$$

$$\frac{124}{114} = 1.087, \quad \frac{114}{105} = 1.086.$$

$$(b) \frac{284}{260} = 1.093, \quad \frac{260}{237} = 1.096, \quad \frac{237}{215} = 1.102, \quad \frac{215}{198} = 1.087, \quad \frac{198}{180} = 1.098,$$

$$\frac{180}{164} = 1.096, \quad \frac{164}{149} = 1.099, \quad \frac{149}{137} = 1.088, \quad \frac{137}{125} = 1.096, \quad \frac{125}{114} = 1.096,$$

$$\frac{114}{104} = 1.095.$$

Square root of mean of above values = 1.047.

$$\text{Average decrement for observations (a)} = \sqrt[24]{\frac{313}{105}} = 1.0465.$$

$$\text{, , , , (b)} = \sqrt[22]{\frac{284}{104}} = 1.0475.$$

Mean decrement,  $\delta = 1.047$ .

$$\lambda = \log_e \delta = 0.0459.$$

$$\text{Ratio, } t/\lambda = 79.5.$$

Altogether six results were obtained for the galvanometer on open circuit, and a corresponding set for closed circuit. The experiments were made by first adjusting the controlling field until a suitable period was obtained ; this was done by moving the controlling magnet, which rested on the bench on which the galvanometer stood, up to or away from the instrument. The period and decrement were then observed with the galvanometer on open circuit ; the terminals of the galvanometer were then short-circuited, and a fresh observation of the period and decrement made. The initial deflexion was in all cases given to the needle by bringing a weak magnet into its neighbourhood, and the needle was started swinging by the sudden removal of this magnet. The results obtained are tabulated below (Table IV.) and plotted as a curve in fig. 4.

These results show that the ratio  $t/\lambda$  is constant for all the periods observed—from 2.5 to 16.5 seconds—when the galvanometer coils are on open circuit. When, however, the terminals are short-circuited, we see, in the first place, that the damping is increased, showing that eddy-current damping has been introduced, and secondly that the ratio  $t/\lambda$  is no longer constant, but increases with the period, *i. e.* with a decrease in the strength of the controlling field, becoming, however, constant at the higher periods. It is evident, therefore, that the alteration in the ratio is due to the eddy-current damping : and, moreover, of the three ways in which it has been pointed out the eddy-current damping may be affected, only the first is consistent with a decrease in the value of  $t/\lambda$  as the period decreases ; for both the self-induction of the galvanometer-coils and change in their resistance due to a rise in temperature caused by the induced currents would cause the ratio to increase as the period decreased. *We must therefore conclude that the change in the ratio  $t/\lambda$  is due to an alteration in the*

Fig. 4.

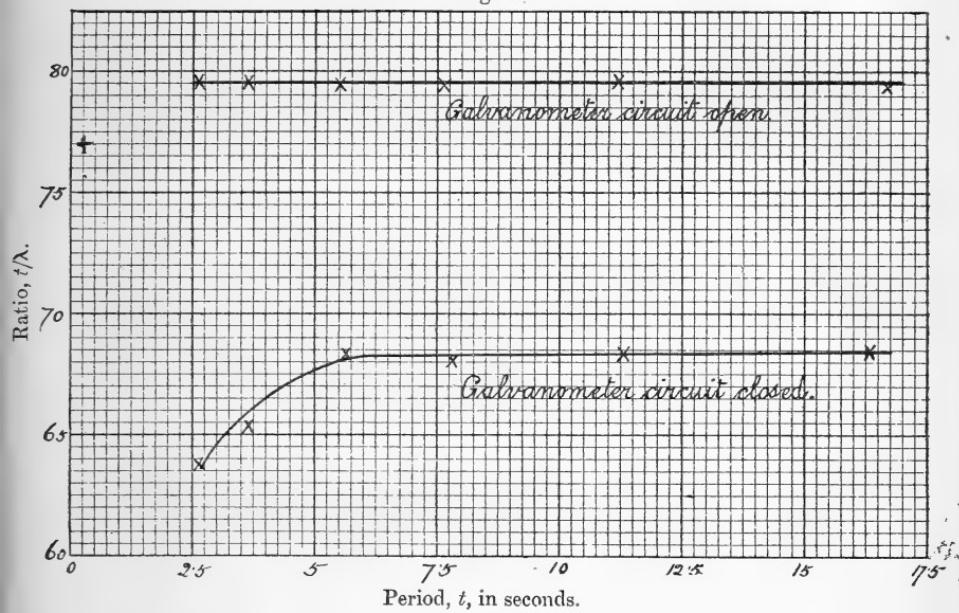


TABLE IV.

Galvanometer Circuit open.					
Experiment	Observed Period = $t$ .	Undamped Period = $T$ ,	Decrement = $\delta$ .	Log $e \delta = \lambda$ .	Ratio $t/\lambda$ .
a .....	2.66	2.66	1.034	0.0344	79.6
b .....	3.65	3.65	1.047	0.0459	79.5
c .....	5.52	5.52	1.072	0.0695	79.4
d .....	7.64	7.635	1.101	0.0962	79.4
e .....	11.18	11.17	1.150	0.140	79.6
f (corrected) }	16.70	16.66	1.233	0.209	79.4

Galvanometer Circuit closed.

a .....	2.66	2.66	1.0425	0.0417	63.8
b .....	3.65	3.65	1.057	0.0560	65.3
c .....	5.70	5.70	1.087	0.0834	68.3
d .....	7.78	7.775	1.121	0.114	68.1
e .....	11.27	11.26	1.180	0.165	68.3
f (corrected) }	16.30	16.26	1.269	0.238	68.5

*strength of the swinging needle produced by altering the strength of the controlling field.*

It will be noticed that although all the experiments agree in showing that  $t/\lambda$  is not a constant, yet the law of its variation is different in different galvanometers. It is evident when we consider what is the cause of this variation, that this might be expected; for the law must be dependent on the construction of the galvanometer and the conditions under which it is tested. The problem is further complicated by the fact that astatic combinations are generally used. The variation in the ratio will depend upon the alteration in strength in each of the magnets of which the combination is composed: and since some of these magnets may be nearer the controlling magnet than others, they will be more affected by altering the position of the controlling magnet. It is, moreover, possible that one of the magnets in the astatic combination may be more favourably situated, by being near metal parts of the instrument, for example, for producing eddy-currents, in which case any changes in its strength will have a proportionately larger influence on the total change in the eddy-current damping. In addition, the change in the strength of any particular magnet will depend upon its initial magnetization, on the steel of which it is made, and also to a certain extent on its previous history. When we remember, further, that the percentage change in the value of the ratio  $t/\lambda$  depends upon how much of the damping is due to eddy-currents and how much to the other causes, viscosity of the air and the suspension, we see that we may expect the ratio to vary in a very great number of different ways.

My thanks are particularly due to Mr. T. Mather for advice as to carrying out the experiments, which were made at his and Prof. W. E. Ayrton's suggestion.

#### LVIII. *Notices respecting New Books.*

*Ueber die Mathematische Theorie der Elektrodynamischen Induction,*  
von RICCARDO FELICI. Uebersetzt von Dr. B. DESSAU. Heraus-  
gegeben von E. WIEDEMANN. Leipzig: Wilhelm Engelmann,  
1899: pp. 1-121.

**T**HE publishers of Ostwald's *Klassiker der Exakten Wissenschaften* certainly deserve the gratitude of all students of physical science for bringing within their reach many of the classical memoirs which are not always easily accessible. The volume before us forms No. 109 of the series, and consists of a translation of Felici's three papers on the mathematical theory of current-induction. As the editor justly remarks, the title is somewhat inadequate, for the memoirs contain not only an attempt to formulate the theory of

the phenomena considered, but also a careful account of Felici's celebrated experiments on this subject. It is probably in connexion with his experimental researches rather than his theoretical work that the name of Felici will go down to posterity. The dates of publication of the three memoirs fall between 1854-55. Considering the enormous advance which has been made since that time, it is hardly to be wondered at that Felici's interpretation and mode of statement of certain phenomena partake of an archaic character: more especially is this the case in the last memoir, which is concerned with the so-called "unipolar" induction. The short sketch of Felici's career at the end of the book fitly concludes this reprint of his papers.

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## LIX. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 502.]

March 7th, 1900.—J. J. H. Teall, Esq., M.A., F.R.S., President, in the Chair.

THE following communication was read:—

1. 'Notes on the Geology of Gilgit.' By Lieut.-Gen. C. A. McMahon, F.R.S., F.G.S.

This paper is based on observations in the field made by Capt. A. H. McMahon, C.S.I., C.I.E., F.G.S., and Capt. J. R. Roberts, I.M.S., and on the petrological examination of the specimens sent home by them. It is divided into three parts. Part I. refers to the work of previous observers, and embodies a brief petrological description of the four granites and aplite intrusive in the sedimentary rocks of Gilgit. Part II. consists of a topographical account of the Gilgit rocks from Askole and Nanga Parbat on the south to the northern passes leading into the Russian Pamirs. Part III. recites the author's conclusions from the facts recorded in the paper. Briefly stated, they are as follows:—

That at one period in the elevation of the Hindu Kush the strata were thrown into a series of folds and compressed into a series of uniconcinal beds with a vertical dip.

That the direction of the main drainage of the area was determined before, or at the commencement, of the last series of earth-movements that crumpled up the strata.

The sedimentary rocks were profusely invaded by granite and diorite, and profoundly metamorphosed by contact-action.

As regards the age of the rocks, the author gives his reasons for identifying the Gilgit limestones with the conformable Carbo-Triassic series of the Himalaya. This series was mapped by Mr. R. Lydekker, F.R.S., in the neighbouring district of Kashmir, and it has been traced up to the border of Gilgit. Sir Martin Conway's specimens, reported on by Prof. Bonney and Miss Raisin, enable the author to connect it with the limestones of Gilgit. From this correlation the author concludes that the oldest rock in the Gilgit

area is of Silurian or Lower Carboniferous age, and that the most recent are of Triassic or even later age. As all the granites are intrusive in the most recent beds, it follows that the granites are younger than the Trias. The author gives his reasons for believing that the oldest granite was erupted while the crumpling of the Gilgit rocks was in progress; but that a portion, at all events, of the younger granites was erupted after the crumpling had taken place.

The author offers an hypothesis to explain certain structures found in the Gilgit granites, including the granophytic structure so common in them.

All the Gilgit granites, the author believes, came from the same igneous reservoir, the differences in them being due to gradual and progressive silification caused by the gradual crystallizing-out of the comparatively basic minerals: the process extending over a long period of time measured in years.

## LX. *Intelligence and Miscellaneous Articles.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,

**I**N the December number of the Philosophical Magazine for 1891 will be found a table of Zonal Spherical Harmonics, published by Professor Perry. Some time ago I had occasion to use these tables and found that in one or two places the values given were erroneous. My work did not involve  $P_7$ , but the test I applied to the others was severe, as is shown by some of the corrections being quite small. I have checked the values I send several times, and Mr. H. F. Skey has also kindly checked them for me.

I am, &c.,

Care of Surveyor General,  
Wellington, New Zealand,  
Feb. 23, 1900.

C. COLERIDGE FARR.

### *Numerical Corrections to Professor Perry's Table of Zonal Spherical Harmonics.*

In $P_2$ angle 76, for	-4112	recd	-4132.
$P_4$ "	47	"	-4252 "
$P_4$ "	68	"	-0650 "
$P_4$ "	70	"	+0038 "
$P_6$ "	7	"	+8476 "
$P_6$ "	19	"	+1347 "
$P_6$ "	25	"	-2053 "
$P_6$ "	47	"	-0645 "
$P_6$ "	66	"	+2996 "
$P_6$ "	68	"	+2605 "
$P_6$ "	71	"	+1786 "
$P_6$ "	73	"	+1144 "
$P_6$ "	77	"	-0284 "
$P_6$ "	86	"	-2811 "

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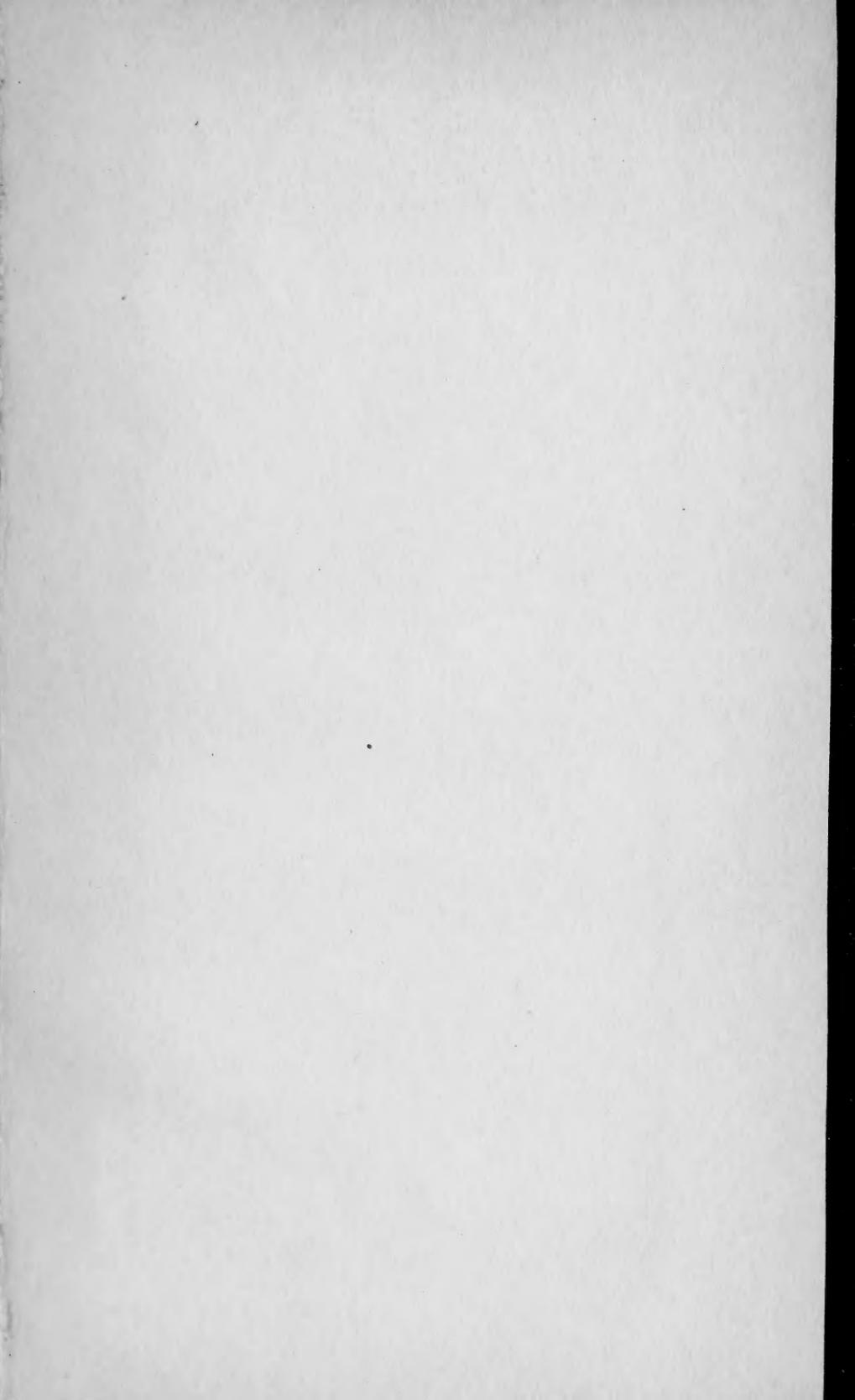
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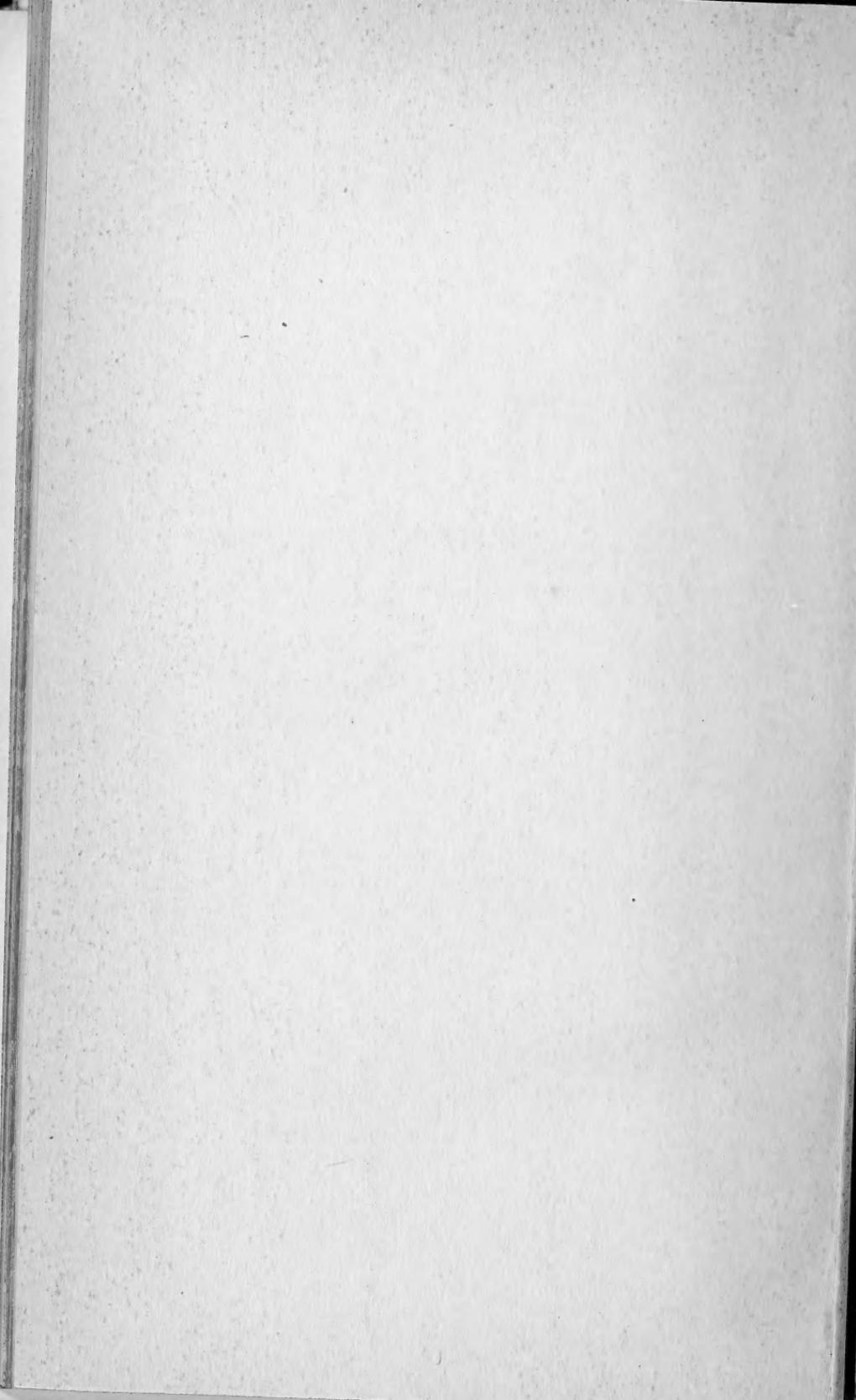
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